RECEIVED
MAY 2 - 1946
O. S. U. LIBRARY

I. C. 7341

FEBRUARY 1946

UNITED STATES
DEPARTMENT OF THE INTERIOR
HAROLD L. ICKES, SECRETARY

BUREAU OF MINES
R. R. SAYERS, DIRECTOR

INFORMATION CIRCULAR

SURVEY OF LITERATURE ON THE METALLURGY OF ZIRCONIUM

BY

W. J. KROLL AND A. W. SCHLECHTEN

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

Digitized by Google

Original from
THE OHIO STATE UNIVERSITY

I. C. 7341,
February 1946.

INFORMATION CIRCULAR

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

LITERATURE SURVEY OF THE METALLURGY OF ZIRCONIUM[1]

By W. J. Kroll[2] and A. W. Schlechten[3]

CONTENTS

		Page
1.	Introduction	2
2.	Extraction from ore	3
	Volatilization of silica	3
	Acid treatment	3
	Fluxing with alkalies	4
	Fluxing with sodium sulfate or sodium bisulfate	4
	Chlorination	4
	Reaction with hydrofluoric acid or fluorides	5
	Miscellaneous processes	5
3.	Production of zirconium metal	5
	History	5
	Reduction of chloride or double chloride with sodium, calcium, or magnesium	7
	Reduction of oxide with calcium, magnesium, or aluminum	7
	Reduction of double alkali fluorides with sodium or aluminum	
	Reduction of oxide with carbon or the carbide with oxide	8
	Reduction of double fluoride or double chloride by fusion electrolysis	8
	Reduction from aqueous solutions by electrolysis	8
	Reduction of halides by the hot-wire dissociation methods	8
	Methods for making malleable zirconium	9
4.	Zirconium alloys	10
	Copper-zirconium	11
	Magnesium-zirconium	12
	Aluminum-zirconium	13
	Silicon-zirconium	14
	Zirconium carbide	14
	Zinc-zirconium	15

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7341."

2/ Consulting metallurgist, Northwest Electrodevelopment Laboratory, Bureau of Mines, Albany, Oreg.

3/ Associate metallurgist, Northwest Electrodevelopment Laboratory, Bureau of Mines, Albany, Oreg.

Generated on 2024-09-19 15:45 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

CONTENTS (Cont'd.)

		Page
4.	Zirconium alloys (Contd.)	
	Zirconium-iron group metals	15
	Miscellaneous alloys	16
5.	Zirconium halides	16
	Zirconium chloride	16
	Zirconium iodide and bromide	18
6.	Other zirconium compounds	18
	Sulfides	18
	Phosphides	19
	Nitride	19
7.	Uses of zirconium and its compounds	19
8.	Bibliography	22

1. INTRODUCTION

This report on the bibliography of zirconium has been confined to those publications and patents that appear to be useful in the commercial development of the metal, both the malleable and the nonmalleable. The methods of production have been stressed and special attention has been given to the alloys. Compounds of importance, like the oxide and chloride, for the manufacture of the metal or of the alloys have been considered. The use of the oxide in refractories and in the glass and porcelain industries has been omitted.

The present survey is critical; that is to say, an attempt has been made to evaluate the effectiveness of suggestions made in the literature. The exhaustive work of Marden and Rich, Bureau of Mines Bulletin 186, published in 1921, has been taken as a base to start from with the intention of bringing the subject up to date with material published in the last 24 years. During this time there was considerable advance in the preparation of the metal and its alloys, and in the development of new uses. On the other hand, there was little progress in the methods of decomposing the ores, so that the chapter on this latter phase is necessarily short.

The original purpose of this survey was to check the literature before starting an investigation on the possible use of zircon sand as a raw material for making malleable and nonmalleable zirconium metal as well as for making zirconium alloys.

It is worth while at the very beginning of this report to emphasize the similarity of zirconium and beryllium, as the metallurgy of both metals is almost identical. This will be seen in the description of the reduction methods for the chloride, oxide, and double fluoride, as well as the fusion electrolysis of the compounds. Ideas used in the metallurgy of one of these metals are generally transferable to the other.

Generated on 2024-09-19 15:44 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

2. EXTRACTION FROM THE ORE

The chief problem in the treatment of zirconium ores is the decomposition of the silicate, and it was found that most processes described in the literature refer to the treatment of silicate. The methods of decomposition of the ores may be divided into the following groups:

1. Volatilization of silica.
2. Acid treatment.
3. Fluxing with alkalies.
4. Fluxing with sodium sulfate or sodium bisulfate.
5. Chlorination.
6. Reaction with hydrofluoric acid or fluorides.
7. Miscellaneous processes.

Volatilization of the silica

Troost(23)[4/] observed that silica is driven off when zircon is melted down with carbon in an arc furnace. Moissan(16) also described a volatilization which he, however, thought was that of zirconium oxide. Thomson(21) volatilized SiO_2 in the arc with carbon. Matignon(15) showed that zircon dissociates at 1,800° C. and that at 2,126° C. the dissociation is complete and pure ZrO_2 remains behind; he worked in absence of carbon. These methods were neglected until recently, when Kinzie and coworkers(11,12) patented methods for the thermal dissociation of zircon combined with the simultaneous preparation of either silicon carbide or zirconium carbonitride using carbon resistor furnaces of the type employed for making silicon carbide. Since the carbon resistor furnace operates in a reducing atmosphere, the reduction of ZrO_2 to a lower oxide seems to be almost impossible to avoid; the treated product has to be roasted in air to obtain ZrO_2. Kinzie claims that in this way an oxide better than 98 percent pure can be made from siliceous ore. Recent publications of Zintl(26,27) indicate that the silica can be driven off as silicon monoxide, either by mixing the ore with silicon and heating at a high temperature or by operating with this mixture in a vacuum at lower temperature. The volatilization of SiO has been frequently reported, and it is probable that in the reduction of zircon with carbon at high temperatures this compound is produced from the silica either directly or by reaction with silicon.

Acid Treatment

The acid treatment of the ore recommended by Marden and Rich must start from a material that has been suitably prepared for attack by acids. Suggestions have been made to sinter(17) the ore or to melt(18) it with calcium oxide, gypsum, or calcium chloride(8); or to quench it from high temperatures(14). As to the acids used, sulfuric or hydrochloric has been

4/ Figures in parentheses refer to items in the Bibliography at the end of this circular.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

recommended by Trapp(22) and by Schmid(18). The sulfates are roasted, and the waste SO_2 may be reclaimed as indicated by Auer(6). Extraction with hydrochloric acid offers the possibility of separating iron and aluminum by the formation of $ZrOCl_2 \cdot 8H_2O$, which is easily precipitated from concentrated hydrochloric solutions. The conditions under which this compound forms have been investigated by Schmid(18) and by Simonova(19). A combined hydrochloric-sulfuric treatment is recommended by Franco-Brezilienne(7). Ullman(24) has reviewed the processes for extracting zirconium from ores. He states that in the sulfuric acid process the ore is treated in the form of fine powder with hot sulfuric acid 1:2. The solution is diluted and the silica filtered off. Sulfuric acid is then added and the solution concentrated to crystallize iron-free sulfate $Zr(SO_4)_2 \cdot 4H_2O$. The crystals are redissolved and precipitated as basic sulfate $Zr_4(SO_4)_2(OH)_{10} \cdot 15\ H_2O$. This salt is roasted to oxide. Alternatively the sulfate may be precipitated with K_2SO_4 as the complex double sulfate of potassium of the formula:

$$(ZrOSO_4)_3 \cdot K_2SO_4 \cdot 8H_2O.$$

Fluxing with Alkalies

Fluxing with alkalies is commonly used for making zirconium oxide for the enamel, glass, and porcelain industries, which want a product containing some alkali(13). In melting or sintering with alkalies, zirconate is produced in addition to silicate. Imperial Chemicals(9) recommends a treatment with sulfuric acid after fluxing. Bozel-Maletra(3) suggests treating the zirconate solution in an autoclave under pressure to hydrolyze it. Acid decomposition of the zirconate is generally recommended by Auer(5) and by Karl(10). A variation of the alkali fluxing method is given by the Ceramic Industry(4); it proposes to flux the ore with soda ash and borax, dissolve the sodium zirconate-silicate thus formed in water leaving the iron and titanium behind, then crystallize to separate the zirconate from the silicate. Ullmann(24) describes the alkali-fluxing process as follows: The ore is melted with 90-94 percent NaOH at 850° C. Sodium silicate goes into solution on leaching, and a sodium silicozirconate remains undissolved. By prolonged leaching, more sodium silicate is extracted. The residue is hydrolyzed, filtered, and dried. It yields an oxide of the approximate composition: 80-84 percent ZrO_2, 8-12 percent SiO_2, 4-6 percent Na_2O, which is suitable for use in the enamel industry.

Fluxing with Sodium Sulfate and Sodium Bisulfate

The fluxing of zirconium ore with sodium sulfate and bisulfate has been fully described by Marden and Rich in Bureau of Mines Bulletin 186, already cited, and no further progress has been made since.

Chlorination

Chlorination of the ore offers some striking advantages for the elimination of impurities, since iron and alumina can be eliminated by precipitation

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

of the zirconium as oxychloride, while the retention of silicon and titanium can be avoided by using a heated condenser. Alexandrov(2) studied the chlorination of ore after adding carbon. He obtained a 90-percent chlorination in 6 hours at 800° C. Teichmann(20) proposes to chlorinate the ore and to use the hydrochloric acid formed in the hydrolysis of the zirconium chloride to leach the undecomposed residues after a thermal treatment.

Reaction with Hydrofluoric Acid or Fluorides

Nothing can be added to the methods of breaking down the ore with hydrofluoric acid, alkali fluorides, or $CaF_2 + H_2SO_4$ as described by Marden and Rich.

Miscellaneous Processes

Among the miscellaneous processes the chlorination of the carbide looks most promising. The carbide is sold at reasonably low cost, and its chlorination is said to be easy. Some authors claim that it can be done below 500° C., and others that the chlorination temperature depends on the physical condition of the carbide. The commercial product is generally about 88 percent zirconium and contains up to 6 percent Al, Si, Fe, and Ti combined. Silicozirconium (about 38 percent Zr), which is the cheapest zirconium alloy, can also be chlorinated, but large quantities of $SiCl_4$ are produced as a byproduct. Ferrozirconium is available at low cost, but the separation of much $FeCl_3$ from $ZrCl_4$ constitutes a problem in itself. Carbon tetrachloride permits chlorination of the ore at low temperature, but the cost is high. Sulfur chloride has also been suggested, since it works at low temperatures, but separation of the sulfur compounds from the $ZrCl_4$ offers some difficulties. These methods are discussed in detail under section 5, Zirconium Halides.

The treatment of eudialite is the subject of patents by Yuz'ko(25) and by Agriomati(1). The zirconium content of the ore may be extracted with HCl and then precipitated from the slightly acid solution with SO_2, or the ore may be brought into solution with strong SO_2 and zirconium precipitated by dilution.

Little information is available about the removal of impurities contained in solutions, beyond what has been published by Marden and Rich. Bosel-Maletra(3) purifies the precipitate after igniting at 400° C. by extraction of the iron with HCl. Removal of the iron by nascent hydrogen or ferro-ferri cyanides is recommended. The problems involved in the separation of hafnium have been carefully investigated, but since hafnium does not interfere with most uses made of the metal or its salts, there is no great interest in such a separation.

3. PRODUCTION OF ZIRCONIUM METAL

History

Berzelius(30) in 1924 reduced potassium-zirconium fluoride with sodium and obtained a zirconium powder, probably mostly lower oxide. Troost(63)

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

repeated his experiments in 1865, and in addition used the following methods: Reduction of gaseous $ZrCl_4$ with sodium or magnesium, reduction of $NaCl-ZrCl_4$ with either magnesium or sodium; reduction of $2NaF \cdot ZrF_4$ with aluminum, and fusion electrolysis of double fluoride and double chloride. He obtained an amorphous metal having a specific gravity of 4.15, indicating that it may have been lower oxide only, and a brilliant crystalline material, made by aluminum reduction of double fluoride, which was mostly aluminide and was contaminated with 6 percent Al and 3 percent Si. In the fusion electrolysis of the double chloride or fluoride he obtained some brilliant metal particles in the form of crystals which were readily attacked by water. Neither Berzelius nor Troost made a pure metal that displayed malleability and corrosion resistance. The first to make such a material were Lely and Hamburger(53) in 1914, who improved the old "gun-barrel" method by operating in a sealed pressure bomb. They obtained from the reaction of resublimed zirconium chloride and sodium a malleable metal in pellets.

Weiss(71) tried in 1910 to drive off the aluminum contained in the metal made by reduction of the double fluoride with aluminum, by remelting the metal in an Arsen vacuum furnace and also in a vacuum arc furnace; but the metal, although it was 99.5 percent pure, was still brittle. These experiments were repeated in 1921 by Marden and Rich(55), who also used the Arsen vacuum furnace and obtained results similar to those of Weiss. The same authors succeeded in making a 99.5-percent metal by aluminum reduction of the oxide with the addition of chlorates, but the yield was poor and the metal brittle. It was not until 1925 that van Arkel, de Boer, and Fast introduced the iodide dissociation method, derived from similar methods already used for making boron, silicon, or tungsten from chlorides as was done by Weiss. They used a hot wire glowing in an atmosphere of iodide, which is more readily dissociated than the chloride. For the first time a compact, malleable metal was obtained that displayed the real properties of the element, and the fact was fully recognized that the embrittlement was caused by the presence of minute quantities of gases, mainly oxygen and nitrogen.

At present, zirconium metal is produced commercially in this country by three companies: The Foote Mineral Co., Philadelphia; the Titanium Alloys Manufacturing Co., Niagara Falls, N. Y.; and the Metal Hydrides Co., Beverley, Mass. The last two firms also sell master alloys.

The main methods for making the metal, as described by the literature, are the reduction of:

1. Chloride or double chloride with sodium, calcium, or magnesium.
2. Oxide with calcium, magnesium, or aluminum.
3. Double alkali fluorides with sodium or aluminum.
4. Oxide with carbon or the carbide with oxide.
5. Double fluoride or double chloride by fusion electrolysis.
6. Aqueous solutions by electrolysis.
7. Halides by the hot-wire dissociation method.

Generated on 2024-09-19 15:44 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Reduction of Chloride or Double Chloride with Sodium, Calcium, or Magnesium

Lely and Hamburger(53) made malleable zirconium in pellets by reducing freshly sublimed chloride with sodium in a bomb. Their equipment was superior to that of Podzus(59) who worked with a similar mixture. The Lely method was used later by Hunter and Jones(48), and it is still employed commercially in this country. Due to the enormous pressures which are momentarily developed the size of these bombs is small, and the method has, therefore, some definite limitations.

The magnesium reduction of the chloride or double alkali chloride, which was introduced by Troost(63), has been recently improved and made commercial by von Zeppelin(67). A mixture of $NaCl$-$ZrCl_4$ and magnesium turnings is heated in an iron pot by applying the heat slowly to the bottom. The mixture melts quietly, partly by the heat of reaction. The clear salts on top ($NaCl.MgCl_2$) are decanted from the black bottom cake containing the metal. The latter is broken up, leached with water, leached with HCl, and dried. Violent explosions may take place when zirconium is dried, even in a vacuum, and von Zeppelin(67) gives special advice on how to get a nonpyrophoric material in this operation. The elimination of the magnesium is almost complete, despite the fact that it alloys with zirconium as shown by Nowotny(56). Magnesium-zirconium alloys of any composition can be made in a similar way. In his French patent, von Zeppelin suggests the use of a vacuum while reducing plain $ZrCl_4$ with magnesium, which is the same method already described by Cooper(34) for the sodium reduction of $ZrCl_4$.

Reduction of Oxide with Calcium, Magnesium, or Aluminum

The calcium reduction of the oxide proposed by Wedekind(68) and used later by Ruff(61) and by Kiernan(49) has been checked by de Boer(40). Kiernan(49) describes also the vacuum degassing and sintering of zirconium powder. Kroll(52) developed the calcium reduction method by operating under argon in a calcium chloride bath at substantially atmospheric pressure. Not all the oxide can be reduced, because of the equilibrium between ZrO_2 and calcium, so that the metal retains some oxygen and becomes brittle. A metal better than 99.5 percent can be made in this way. Alexander(28) reduces the oxide with calcium hydride in a vacuum. The advantages of this method compared with the direct reduction with calcium are not apparent, and the resulting metal is brittle, like that made by direct calcium reduction. Marden and Rich(55) made a 99.5-percent metal by aluminothermic reduction with chlorate addition, but the yield was poor. The magnesium reduction of the oxide in a sealed vessel as recommended by Marden(54) does not seem practical, since ignited magnesia is very difficult to remove even with strong acid and there is no readily fusible solvent available for fluxing magnesia.

Reduction of Double Alkali Fluorides with Sodium or Aluminum

Reduction of the double fluoride with sodium was the standard process for making a high-purity metal in Europe until calcium-reduction of oxide

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

was substituted. Sodium reduction produces a very fine, colloidal metal. De Boer(40) studied this last method carefully.

Aluminum reduction of the double fluoride as used by Weiss(71) and by Marden and Rich(55) yields aluminide of various compositions. The aluminum can be driven off at high temperature in a vacuum, but the metal remains brittle.

Reduction of Oxide with Carbon or Carbide with Oxide

Carbon reduction of the oxide produces, when operating with a carbon deficiency, a material containing interspersed metal, according to Dawihl(35) and Bozel-Maletra(31). The former claims that a mixture of carbide and metal is obtained; the metal contains only 70 percent zirconium but could be refined on a CaO layer.

Rohn(60) suggests that metal oxides be allowed to react with carbide in a vacuum. Among those suggested are zirconium and columbium. Recently Balke(29) confirmed that the latter metal can be made in such a manner. Data for zirconium, however, are lacking.

The reaction between carbon and ZrO_2 has been studied by Friedrich and Sittig(46), who found a reduction half way to the compound ZrO when operating at 1,200° C. Above this temperature they obtained carbide. Previous authors doubtless have been mistaken by the appearance of lower oxides which look like a metal.

Reduction of Double Fluoride or Double Chloride by Fusion Electrolysis

Fusion electrolysis of the double fluoride, as suggested by Troost(63), has been repeatedly recommended by subsequent investigators like Marden and Rich(55) and Driggs and Lilliendahl(42). Oxide has to be added to avoid anode effect and as a result, much lower oxide or colloid is made.

Fusion electrolysis of the double chloride, as recommended by Troost(63), has recently been used again by Plotnikov(58), who worked also in an $AlCl_3$-KCl-NaF bath and added ZrO_2. His metal probably was contaminated with aluminum. His best metal was 92.9 percent, indicating the presence of lower oxide.

Reduction of Aqueous Solutions by Electrolysis

Aqueous electrolysis has been tried by Bradt and Linford(32), who found a zirconyl-sulfate bath the most successful. Little hope can be seen for this method due to the great chemical activity of zirconium.

Reduction of Halides by Hot-wire Dissociation Method

Halide dissociation methods derive from previous attempts to dissociate chlorides, like those of boron(69) and silicon, in an arc or spark; this was also done in the presence of hydrogen as a reducing agent. Weiss(70) used the hot-wire method to reduce tungsten chloride. The reducibility

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

of $ZrCl_4$ on a hot wire has been contested by van Arkel(65) after Fischvoigt(45) had obtained some deposits. These deposits were attributed by van Arkel to nitrides, oxides, or carbide due to impure hydrogen used in the experiment. Burgers(33), however, showed later that by substituting a zirconium wire for tungsten and by operating at high temperature zirconium could be grown on the wire. Tungsten forms a low-melting eutectic with zirconium, which makes the use of tungsten impossible at such high temperatures as those required in decomposition of the chloride. Pure tantalum has been made recently by dissociation of the chloride.

The merit of the processes of van Arkel, de Boer, and Fast of the Philips plants in Holland is the use of the iodide, since this compound is more readily dissociated than the chloride. The method is described in a number of publications (38, 41, 43, 57, 64), and it has been extended to titanium and hafnium.

Methods for Making Malleable Zirconium

Lely and Hamburger(53) were the first to produce malleable zirconium. They employed resublimed chloride which they reduced with sodium in a bomb. Such a method can be used for making malleable metal if one takes care that the chloride is not exposed for any length of time to the moisture of the air, which will react quickly with the solid chloride particles due to their large surface and introduce oxygen. The irregular pellets produced cannot be processed by powder metallurgical methods but could be remelted in a vacuum arc furnace as has been done with titanium(50). However, the bomb method has definite limitations as to size, and it does not seem possible to improve the process in this regard.

The Philips process(57) developed by van Arkel(65) and de Boer and Fast(41) permits production of a high-purity malleable metal by dissociation of the iodide. This method also has definite limitations as to the size of the equipment, since the necessary current input is a function of the diameter of the wire, which increases as the operation proceeds. Heat dissipation becomes a problem with thick wires and heavy currents.

The embrittlement of zirconium is due, as shown by van Arkel and associates, to the pick up of minute quantities of gases, mainly hydrogen, nitrogen, and oxygen. The gases are introduced in the usual reduction processes either by handling the reaction mixture at elevated temperature in contact with air, by using impure noble gases as a seal, or by the aqueous methods used in extracting the powder. The oxide skin on finely divided powder may be sufficient to cause embrittlement. In oxide reductions the equilibrium involved causes a pick up of oxide by the reduced metal.

The role of the individual gases as a contaminant of zirconium is described in the literature as follows:

Hydrogen. - The behavior of hydrogen is also described in chapter 6 of this article. Van Arkel(66) states that all of the hydrogen can be pumped

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

off at 1,500° C. in a good vacuum and the metal brought back to malleability. The action of hydrogen on the transformation point has been studied by de Boer(36). Hydrogen shifts the transformation point slightly to higher temperatures and makes it more sluggish. The solubility of hydrogen increases suddenly at this point. Hägg(47) examined the system hydrogen-zirconium by X-ray methods and found five phases. The solubility of hydrogen in alpha zirconium is 5 atomic percent.

Oxygen. - Oxygen in fairly large amounts does not impair the hot malleability of zirconium, but the metal is brittle in the cold state. A lower oxide is formed, and according to Fast(44) 40 atomic percent oxygen is soluble in zirconium. It shifts the transformation point to higher temperatures and makes the transformation sluggish. This has been shown by Schulze(62), Zwikker(72), and de Boer(39). The last states that oxygen-free zirconium has a sharp transition point at 862 + 5° C., while it may be shifted to 1,150° C. and more by the presence of oxygen, as shown by resistance measurements, and the temperature interval from the start to the end of the transformation increases considerably.

Oxygen may be introduced by annealing, mainly with thin sections, due to back diffusion of the oxide skin into the metal. Van Arkel(66) showed that this could be partly avoided by pickling with HF before annealing. According to de Boer(37), the oxygen can be shifted within a wire of zirconium by passing a direct current through it at a temperature of about 1,500° C. The oxide migrates to the anode by "electrolysis", a phenomenon shown by some other authors with other alloys.

Nitrogen. - Nitrogen, according to Zwikker(72), also shifts the transformation point. Fast(44) studied the influence of this gas and claims that it is not released by heat. However, van Arkel(66) thinks that small amounts at least are given off at elevated temperatures in a vacuum.

Other Impurities. - The embrittlement of zirconium by nongaseous alloying elements has been studied superficially. De Boer(40) finds that silicon is harmful while van Arkel(66) thinks that small amounts of silicon as well as iron may be tolerated. Van Arkel(66) states that aluminum makes malleable alloys. The same author shows that titanium, which forms solid solutions over the whole range, hardens zirconium. Hafnium alloys are malleable. Tin should be avoided. The hot malleability of zirconium is probably not impaired by numerous other metallic additions, since the metal most likely behaves in this regard like titanium(51).

4. ZIRCONIUM ALLOYS

Recent investigation deals with alloys of heavy and light metals with zirconium, with equilibrium diagrams, X-ray structure, mechanical

Generated on 2024-09-19 15:52 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

properties, corrosion, and uses. The last will be considered partly here, partly in chapter 7.

The most interesting zirconium alloys are those with copper, which are age-hardenable as well as good conductors of electricity; those with magnesium, which have good mechanical properties, high elongation, and excellent corrosion resistance; and those with iron and silicon, used as scavengers for steel and for grain control. Hansen(97) in his textbook on binary alloys gives information about the following zirconium alloys: Al, Pb, B, Fe, Hf, C, Cu, Mg, Ni, P, Hg, S, Se, Ag, Si, U, Ti, H, W, Sn.

The Metal Hydrides Co. and the Titanium Alloys Manufacturing Co. make master alloys, chiefly with copper.

Copper-Zirconium Alloys

In 1929 Allibone and Sykes(75) studied a number of zirconium-bearing alloys, among which they examined copper-zirconium with up to 20 percent Cu. In particular, they checked the microstructure, Brinell hardness, tensile strength, elongation, and the age-hardening properties.

Hensel(101) patented such alloys and claims that the 0.93 percent Zr alloy hardens by aging as follows: when quenched from 950° C., it had a Hardness of Rockwell B 10; after aging 8 hours at 450°, the hardness increased to Rockwell B 59. The conductivity as quenched was 48 percent; when aged 16 hours at 450° C, it was 76 percent.

Pogodin-Schumova(125,126) studied the equilibrium diagram and properties of the Cu-Zr series. They confirmed the existence of the compound Cu_3Zr, which melts at 1,138° C. and forms a eutectic with 12.90 weight-percent zirconium, melting at 980° C. The solid solubility of zirconium in copper is 1 percent at 980° C., 0.28 percent at 600° C., 0.07 percent at 400° C., and only 0.03 percent at 300° C. A quenched alloy with 1 percent zirconium doubles its hardness on aging. The 1.8-percent Cu-Zr alloy reaches a Brinell hardness of 80 after aging.

To obtain maximum aging effects, Harrington(98) recommends double aging after cold stress.

Ternary and multicomponent alloys have been patented in great numbers. The well-known age-hardening agents used for copper have been combined with zirconium, and a number of these alloys have remarkable properties.

Comstock(88) shows the beneficial effect of zirconium additions to beryllium copper, to which it imparts a greater strength at elevated temperatures. Hensel(102,104) describes how additions of cadmium, silicon, lithium, and magnesium improve copper-zirconium alloys. Combinations of cadmium and zirconium are especially recommended; an example is 0.9 percent Cd and 0.56 percent Zr. The following table gives the properties of such an alloy in the aged condition. As a basis for comparison, the

Generated on 2024-09-19 15:42 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

second column lists similar data for a 2.25-percent beryllium alloy treated for maximum electrical conductivity according to Wilkins(154).

TABLE 1. - Comparison of zirconium-copper and beryllium-copper alloys

	Zr-Cd-Cu	Be-Cu
Hardness, Rockwell B.....	81-87	111
Electrical Conductivity.....	78-81 percent	32-38 percent
Tensile strength.....	78,000 p.s.i.	160,000-180,000 p.s.i.
Yield point.....	73,000 p.s.i.	
Elongation in 2 inches.....	11 percent	4-8 percent
Brinell hardness at 125° C.....	148	
Brinell hardness at 350° C.....	119	

As to specific multicomponent alloys of the copper-zirconium base, the following data have been taken from the literature:

Seri(136) suggests beryllium additions with a certain Be : Zr ratio. Nickel additions in a certain Ni : Zr ratio are proposed by Nippes(119). Many combinations are patented by Hensel(102), especially those with iron-group metals, also those with beryllium, lithium, and tin for welding electrodes. Analogous claims are made by Kelley(108) regarding age-hardenable alloys with iron-group metal additions for electrical apparatus.

Philips(122) advises the use of binary copper-zirconium alloys with 0.02-5 percent Zr for wire in tube manufacturing, since these alloys display about the same conductivity as copper but have 1.5 times its tensile strength.

Quaternary copper-zirconium-nickel-aluminum alloys, as proposed by Nippes(119), with 24 percent Ni, 1.15 percent Zr, and 2.6 percent Al, reach, after aging, a tensile strength of 112,000 lb. per square inch with 18.5-percent elongation.

Methods for production of copper-zirconium are patented by von Zeppelin(147), who reduces $ZrCl_4$ mixtures with magnesium in a copper pot, which he submerges in molten chlorides or flux, and melts down either by the heat of reaction or by additional heating. Belozerskii(81) makes these alloys by fusion electrolysis in a chloride-fluoride bath, using copper as a cathode and melting down the readily fusible eutectic, which he collects at the bottom of the cell. Similar propositions have been made before for titanium-copper.

Magnesium-Zirconium Alloys

These alloys are quite promising, since zirconium is a powerful neutralizer for iron; this effect is used to increase the corrosion resistance of magnesium alloys. However, since zirconium also has other strong intermetallic affinities, it may react back with other constituents of the alloy, and the iron neutralization may be reduced. Therefore, a special

Generated on 2024-09-19 15:53 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

composition is required if the full iron neutralization effect is to be obtained. Zinc is said to be neutral against zirconium, while aluminum and manganese react within the magnesium alloy. Zirconium also increases the elongation and tensile strength of magnesium by grain refining. There are difficulties in introducing zirconium into magnesium, probably due to skin formation on the reduced zirconium particles.

The equilibrium diagram magnesium-zirconium has been studied by Nowotny(120), who found an unstable compound Mg_2Zr and a wide range of solubility. The solid solubility is 0.8 percent at 700° C. and 0.3 percent at 300° C. The corrosion properties of these alloys are described in his paper. Sauerwald(134) patented an alloy with 2.1 to 5 percent Zr.

Methods for introducing zirconium into magnesium are described in the patent literature. Sauerwald(134) stirs the zirconium into freezing magnesium in powder form. Von Zeppelin(146) uses zirconium in a flux, or $ZrCl_4$ dissolved in a flux, which reacts with the magnesium alloy while stirring. Magnesium-Electron(113) proposes introducing the $ZrCl_4$ in form of molded pieces of definite density.

The heat treatment of magnesium-zirconium alloys is the object of some patents by Sauerwald(133). It is difficult to bring the zirconium homogeneously into solution in the alloy. A heat treatment at 150° to 600° C., preferably at 450° C. for 8 hours, causes dissolution.

In complex alloys, care has to be taken that the zirconium is not neutralized by other elements. I. G. Farben(105) claims that the metals Al, Si, Sn, Mn, Co, Ni, and Sb have to be absent, while useful additions which do not react with zirconium are Zn, Cd, Ce, Ag, Tl, Th, Cu, Bi, Be, Pb, and Ca. This restricts the use of zirconium essentially to zinc bearing magnesium alloys.

The grain-refining action of zirconium is used to impede the coarsening influence of other metals such as beryllium. Société Alais Froges (Gauthier) (93) advises the use of Be-Zr additions to magnesium alloys, the former metal having the property of reducing burning during casting.

The corrosion properties of magnesium alloys with cadmium and zirconium have been studied by Obinata(121). Corrosion resistance of Mg-Al alloys is stressed in a patent of Alliages autoprotégés(74). The grain refining action of zirconium is mentioned by Beck(77).

Aluminum-Zirconium Alloys

These alloys do not seem to be of special interest as materials for construction. The binary series have been studied by Allibone and Sykes(75) who also studied the mechanical properties, and the aluminum end of the series has been checked by Fink(91), who determined the crystal structure of the compound Al_3Zr. The solid solubility of zirconium in aluminum is 0.28 atomic percent at 660.5° C. and only 0.05 atomic percent at 500° C.

Canac(87) suggests the use of Al-Mg-Zr alloys with up to 3 percent zirconium for corrosion resistance.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

The light emission of burning Al-Mg alloys with zirconium additions has been examined by van Liempt(141), and a patent by Sarbey(132) concerns the same subject. Such alloys, when rolled or drawn to fine sections and flashed in a bulb with some oxygen, develop more visible light than plain magnesium.

A number of aluminum-zirconium alloys and methods for their fabrication are described by Gmelin(95).

Zirconium with a small amount of aluminum is malleable, and grid wires of this composition have been proposed by Philips(123) for vacuum tube construction.

Silicon-Zirconium Alloys

These alloys are used as scavengers for steels and in combination with boron to control the grain size and improve the mechanical properties and the deep hardening. They are also used to produce "free-machining" sulfur steels. The compound Si-Zr has been identified by X-ray analysis. Literature refers mainly to the methods of fabrication of these alloys.

Wainstein(148), Jeljutin(106), and recently Volkert(145) examined the methods of production. The main difficulty in carbon reduction in the arc furnace is the formation of zirconium carbide, which takes place because of an equilibrium between silicide and carbon when the silicide reaches a composition of more than 50 percent Zr. The carbide formed can be reacted with either silicon or silicide containing more silicon than zirconium, according to Becket(80). Fresh ore rich in SiO_2 can also be used. The addition of calcium carbide or lime permits the production of alloys higher in zirconium, but these contain some calcium. This method, described by Renaux(129), is recommended by Bózel-Maletra(85) and has been checked by Volkert(145). The carbon content can be held below 1 percent. The technical product usually contains 38 percent zirconium, 1 percent aluminum, up to 5 percent iron, and the remainder silicon. Aluminum reduction is also possible, as shown by Jeljutin(106), and silicon itself can be used to reduce zirconia, as shown by Wedekind(151), although SiO compounds may form. The zirconium recovery of these investigators was generally below 50 percent.

Andrieux(76) made the silicide by fusion electrolysis of silicates with ZrO_2 additions.

Deoxidizing alloys with iron-zirconium and silicon have been patented by Becket(79).

Zirconium Carbide

The formation of this compound has been studied by Troost(138), Moissan(117) (who identified it), Wedekind(151,152), Hartmann(99), Mott(118), Friedrich(92), and Weiss(153). Generally an arc furnace was used, and

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

calcium carbide was added. According to Renaux(129), zircon ore can be fused with calcium carbide to form directly ZrC; no calcium remains behind. He used 20 parts of ore, 12 parts of CaO, and 7 parts of carbon. At a temperature as high as that produced in the arc, silicon carbide does not form, or if it does, it breaks down. Even iron and some aluminum volatilizes. The technical product contains about 86 percent zirconium, 12 percent carbon, and the rest silicon, titanium, aluminum, and iron.

The equilibrium between ZrO_2 and carbon has been checked by Prescott(127), who found an equilibrium pressure of 1 atmosphere at 1,657° C. The properties of synthetic carbide have been studied by Nejersson(115) and more specifically by Becker(78). The latter examined the methods of production, structure, density, hardness, strength, melting point, volatility, electrical conductivity, and magnetic and optical properties mainly in connection with possible uses in sintered hard metals. Van Arkel(140) obtained the carbide by dissociation of $ZrCl_4$ on a hot carbon filament.

Zinc-Zirconium Alloys

The equilibrium diagram has been examined by Gebhardt(94) who found no compound, but determined the solubility in the liquid state. The solid solubility of zirconium in zinc is only 0.02 weight-percent at 400° C. There is a eutectic point at 0.1 percent Zr, and the melting point reaches 1,200° C. at 3 percent Zr. These alloys seem to be of no interest.

Zirconium-Iron Group Metals

The iron zirconium equilibrium diagram has been studied by Allibone and Sykes(75), by Vogel and Tonn(144), and by Wallbaum(149). There is a compound Fe_3Zr_2 forming a eutectic with Fe at 16 percent Zr and 1,330° C. Resistance measurements as well as hardness tests, have been made by Sykes.

The ternary diagram Fe-Zr-C examined by Vogel(143) shows that the carbon is tied up by zirconium, which explains the proposal to use zirconium as a stabilizer in 18-8 steels. According to Thum(137), the action of Zr is not favorable for this purpose.

The ternary diagram Fe-Zr-S, established by Vogel(142), discloses the strong sulfur affinity of zirconium. There is a miscibility gap between the sulfide and the iron. A compound, ZrS_2, forms which has a melting point of 1,550° C.

Some uses of zirconium alloys with an iron base are mentioned in the patent literature. Combinations of Fe-Ni-Zr with about 16 percent zirconium, which corresponds to the eutectic, are recommended as welding material for liquid-air tanks by Lentz(112). Armor plates containing carbon and zirconium are claimed by Boehler(82). Magnetic alloys containing iron and zirconium in addition to nickel are mentioned by Raffles(128), Alexander(73), and Krupp(111). Zirconium evidently plays here the same role as titanium.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Zirconium-iron master alloys are used in the steel industries as deoxiders and desulfurizers and for grain control. Boron may be added to produce deep hardening properties in the treated steels.

Sulfur-bearing zirconium steels are "free cutting," as shown by Thum(137).

The nickel-zirconium equilibrium diagram has been investigated by Sykes(75), who also studied the hardness of the alloys. A compound Ni_3Zr has been found. Wallbaum(149) also investigated this system. Pilling (124) attributes the aging of ternary Fe-Ni-Zr alloys to the solid solubility of Ni_2Zr in nickel.

As to the uses of these alloys, they have been proposed by Cooper(89) for cutting tools, for instance in the following compositions: 71-78 percent Ni, 3-4 percent Si, 6-5 percent Zr, 4-12 percent W, and the rest Fe. These alloys were made by aluminothermic reduction of ore. Their hardness is evidently due to the presence of intermetallic compounds. Nickel-zirconium is proposed by Bosch(84) as a sparkplug material. De Boer(90) recommends its use as electrodes in lamps, due to the good strength especially when hot. Rohn(130) claims exhaust valves of the Ni-Fe-Co-Zr composition. Degassing of nickel castings with zirconium has been examined by Hensel(103). Boecker(83) recommends hard alloys with zirconium additions.

The cobalt-zirconium equilibrium diagram has been investigated by Koester(109) and by Wallbaum(149); the latter states that a compound Co_4Zr exists. The considerable magnetism of this compound was checked. McElroy (114) proposes combinations of Co-Cr-W-Zr with up to 10 percent zirconium as cutting tools.

The manganese-zirconium system has been studied by Wallbaum(149) who found the compound Mn_2Zr.

Miscellaneous Alloys

Alloys of the tungsten group with zirconium have been investigated, and a compound of the composition ZrW_2 has been found. Alloys with 10-50 percent tungsten are said by Kamishima(107) not to oxidize. Goyler(96) proposes W-Mo-Cr-Zr mixtures for centrifugal castings, and Hensel(100) makes welding electrodes out of W-Mo-Zr alloys. Schaefer(135) suggests tool alloys with zirconium, tantalum, and tungsten-group metals; Braid(86) proposes the same for dental alloys. Kroll(110) advises the use of similar alloys for light reflectors. Misch(116) studied the compound $ZrBe_2$. Platinum alloys with high corrosion resistance are mentioned by Ruthardt(131). Alloys with 1 percent tungsten were made by Wartenberg(150), who reduced ZrO_2 with dry hydrogen in presence of tungsten powder at 2,500° C. and 5 atmospheres pressure. Zirconium-titanium and zirconium-hafnium form solid solutions over the whole alloying range, as shown by van Arkel(139).

5. ZIRCONIUM HALIDES

Zirconium Chloride

Zirconium chloride may be used for making the metal and its alloys as well as for preparation of the oxide. It can be made by chlorination

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

of the ores mixed with carbon at temperatures above 700° C. The ore can be chlorinated directly with carbon tetrachloride or with sulfur chloride at lower temperatures.

Zirconium carbide can readily be chlorinated with chlorine at temperatures below 500° C., but the physical shape seems to influence the reaction temperature. Burgess(158) chlorinates with HCl and claims that silicon is not chlorinated.

The chlorination of the zircon ore has been described by Alexandrov(155) who obtained a 90-percent extraction of the zirconium at 800° C. in 6 hours with a 17.4-percent carbon addition. Carbon tetrachloride is used by de Boer(160) among others who reacted it with ZrO_2. Picon(166) chlorinates Zr_3S_2 at 280° C. The chlorination of the carbide mentioned by Moissan(164) was used by Staehler(172) and by Wedekind(175).

Rahlfs(167) studied the physical properties of zirconium chloride. It sublimes at 331° C. and melts at 437 ± 2° C. under a pressure of about 25 atmospheres. The vapor-pressure curve can be expressed by the formula:

$$\log p_{mm} = \frac{-2600}{4.57.T} + 12.30.$$

Fischer(162) gives a melting point of 438 ± 1° C. The density of the vapor has been studied by Friend(163), who found abnormal behavior above 500° C. which he attributes to the dissociation to $ZrCl_3$ and liberation of chlorine. Ruff(168) investigated the reducibility of $ZrCl_4$ with metals, especially aluminum, and found that with aluminum at 250° C. a reduction to $ZrCl_3$ occurred. Above 330° C., $ZrCl_2 + ZrCl_4$ is formed from $ZrCl_3$; above 600°, $ZrCl_2$ breaks down to metal and $ZrCl_4$. Fast(161) found that at 1,200° C. dichloride is formed by reaction of the metal with $ZrCl_4$. The dissociation temperature of the dichloride must be still higher. $ZrCl_4$ can be dissociated on a hot carbon filament according to Philips(165) with formation of carbide. The reduction of $ZrCl_4$ with hydrogen in the presence of CO and with the formation of carbide has been described by van Arkel(174).

The vapor pressure of zirconium chloride can be greatly reduced by dissolving it in salts which form double compounds, for example, NaCl. Belozerskii(156) studied the electrical conductivity of the NaCl-$ZrCl_4$ series and found a complex formation. He also examined the melting points of these series(157) and came to the following results: the compounds, 4NaCl and 1 NaCl·$ZrCl_4$, are established. An unstable compound, 2NaCl·$ZrCl_4$, is probable. The melting points are 535° C. for 4NaCl·$ZrCl_4$ and 330° C. for NaCl.$ZrCl_4$. Three eutectics are found at 390°, 220°, and 162° C. This shows that a fusion electrolysis could be run far below 500° C, using these salts, even below 200° C., with multicomponent mixtures.

Generated on 2024-09-19 15:45 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Zirconium chloride reacts on heating with a number of oxides, as shown by Troost(173). Ruff(168,169) examined such reactions and found that the oxides of titanium, iron, molybdenum, and tin are decomposed by $ZrCl_4$, with formation of ZrO_2. Zirconium ores can be freed of iron and titanium by reaction with $ZrCl_4$. Silica is not attacked at low temperatures, but at higher ones ZrO_2 and $SiCl_4$ are produced. Glass is attacked by $ZrCl_4$, a fact that has been acknowledged by Fischer(162).

When dissolved in concentrated hydrochloric acid, the anhydrous chloride forms oxychloride of the formula $ZrOCl_2.8H_2O$. The conditions for an almost quantitative precipitation of this compound have been indicated by Simonova(171). A solution with 318 grams HCl per liter is recommended. The anhydrous chloride can be completely dissociated into oxide by steam at 170°-200° C.

The existence of water-free oxychlorides is admitted by Schmid(170), who claims that the oxychloride, $ZrOCl_2.2H_2O$, splits above 150° into ZrO_2 - HCl but that in a current of HCl a water-free oxychloride of the formula $ZrCl_4.3ZrO_2$ is obtained. The stability of an oxychloride $ZrOCl_2$ up to 300° C. is stated by Ruff(168). The production of anhydrous chloride by drying a solution of $ZrCl_4$ and igniting in HCl seems, therefore, not to promise success, since only a part of the anhydrous oxychloride yields anhydrous chloride. Ruff(169) studied the reduction of $ZrCl_4$ by Al, As, Sb, Pb, Sn, Hg, Bi, P, Mg, and states that Mg reduces the $ZrCl_4$ to $ZrCl_3$.

De Boer(159) reveals some interesting properties of $ZrCl_4$, which forms double compounds with PCl_5. The compound $2ZrCl_4.PCl_5$ boils at 416° C. When PCl_5 is melted with $ZrCl_4$, $SiCl_4$ if present is driven off. The double zirconium-phosphorus compound can be distilled off, and iron and aluminum stay behind as less-volatile double chloride with phosphorus. The zirconium double chloride can be decomposed with NaOH solution.

Zirconium Iodide and Bromide

These compounds are of interest only insofar as they may be used in the dissociation process for making the metal. The dissociation of the tetraiodide has been studied by Fast(161). The physical properties of tetraiodide and bromide are the subject of an investigation by Rahlfs(167). The iodide melts at 499 ± 2° C. and sublimes at 431° C., and the bromide melts at 450 ± 1° C. and sublimes at 357° C. Formulas for the vapor-pressure temperature relation are given.

6. OTHER ZIRCONIUM COMPOUNDS

Sulfides. - Sulfides have been investigated by Strotzer(186) and Picon(182). The first found the following sulfides, which he examined by X-ray diffraction: ZrS_3, ZrS_2, $ZrS_{0.75}$ and lower sulfides. Picon mentions Zr_3S_5 and ZrS_2. He made the sulfides from oxide and H_2S at 1,000°-1,700° C.,

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

while Strotzer used $ZrCl_4$, which he reacted with H_2S. Strotzer measured the dissociation pressures of the higher sulfides.

Phosphides. - The phosphides have been made by Strotzer(185), who gives the following compositions: ZrP_2, ZrP, and subphosphide Zr_3P. The dissociation pressures of the higher phosphides have been measured.

Nitride. - Becker(178) examined the nitride and studied its physical properties. Friedrich(180) prepared the nitride from oxide and carbon in a nitrogen atmosphere at 1300° C. He produced ZrN with 79.3 percent Zr, 12.3 percent N, and 1.5 percent insoluble matter. Cyanonitrides are recommended by Comstock(179) to introduce nitrogen into steels.

Hydride. - Zirconium readily absorbs hydrogen when heated in this gas with embrittlement of the metal, but it gives it off again at elevated temperature. Sieverts(183,184) studied the equilibrium pressures between metal and hydrogen at elevated temperatures. At 900° C., the isobar at 1 atmosphere shows a rapid drop, indicating release of most of the hydrogen. According to van Arkel(187), the gas can be eliminated completely at 1,500° C. in a good vacuum. The maximum absorption of hydrogen corresponds to the formula $ZrH_{1.92}$. The equilibrium pressure is 104mm. Hg at 200° C. and 752 mm. Hg at 800° C. The heat of formation of the compound ZrH is 38.9 Cal. The X-ray structure of the hydride has been studied by Hägg(181). Hägg discloses five different phases in the ZrH_2 system. Five atomic percent hydrogen are soluble in alpha zirconium. The hydride is of some interest because of the uses which have been suggested.

Alexander(176) describes the production of zirconium alloys from the hydride by reaction with oxides. Alloys, Ltd.,(177) suggests employing the hydride for sintering metal powders. The hydride is used for gettering in tube manufacturing; it is sprayed on and thermally dissociated in the tube itself. The hydride seems to be less pyrophoric than the metal and it is shipped dry, while the metal is usually preserved by wetting with alcohol. Zirconium getter coatings have excellent heat dissipating properties.

7. USES OF ZIRCONIUM AND ITS COMPOUNDS

Metallic zirconium is available in two forms, malleable and nonmalleable. The former is quite expensive, and only small amounts are produced commercially; the nonmalleable powder sells for about $7 per pound.

The main uses of zirconium in alloys have been described in chapter 4 of this survey. Master alloys with a copper base are available commercially.

The getter properties of zirconium are used in lamp manufacturing, as described by Fast(197). Zirconium may be applied in powder form or as the hydride to parts that will be heated while the tube is working, or such parts may be made directly of zirconium metal. Vierkoetter(215) uses the metal for gettering tubes. Telefunken(211) operates zirconium parts at a definite temperature in tubes containing hydrogen. De Boer(195) and Philips(205) suggest its use and that of aluminum-bearing alloys for grid

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

wires in vacuum tubes and for the parts of discharge tubes exposed to high temperatures. Light Metals(204) and Hukogawa(200) describe the getter properties of zirconium in detail. Espe-Knoll(196) show where zirconium could be used in tubes. Since zirconium readily reduces alkaline earth metal oxides, it can be used as a reducing agent for barium and similar metals which in themselves have good gettering properties as shown by van Arkel(213).

The excellent light reflection of zirconium metal suggests its use for mirrors, according to Sabine(209). The Allgemeine Elektrizitats Gesellschaft(189) has shown that zirconium causes mercury to wet the surface of iron boilers.

Due to its oxide skin, zirconium, may be used as an electrolytic condenser for rectifiers, according to Philips(206). Thin layers of zirconium offer great electrical resistance, according to Kolligs(203).

The good light emission of burning zirconium in the visible part of the spectrum suggests its use in flashlight powders and photoflash bulbs. Since ZrO_2 is not volatile, the metal was used for smokeless flashlight powders before the introduction of bulbs. Weidkind and Krebs(216) mention the use of zirconium metal mixtures with nitrates. Van Liempt(214) studied the light emission of zirconium alloys; Philips(207) patented the use of the metal in bulbs. Sarbey(210) operated with alloys in much the same way as Philips, but Forrest(198) used a hydride in flash powders.

Zirconium is not suitable for spinnerets, although it has been recommended by Philips(208). In general the good corrosion resistance against hydrochloric acid suggests the use of zirconium metal in chemical equipment. Gillett(199) suggests the specific use for the condensation of hydrochloric acid; he also describes the mechanical properties of the metal.

Zirconium powder ignites at about 210° C. and has been recommended as a primer for ammunition by Chambers(193). The difficulties in handling zirconium powder, which is pyrophoric and usually shipped moistened with water or alcohol, may be overcome by packing it in noble gas containers as claimed by Alexander(188); organic coatings are also recommended.

Zirconium hydride may be added to metal powders that are to be sintered, as shown by Jones(201) and Alloys, Ltd.(190); the nascent hydrogen is said to assist very effectively the sintering. Balke(191) proceeds in a similar way, but in vacuo.

Zirconium has been suggested as a solder for tungsten, molybdenum, and tantalum. Van Arkel(213) tells of the use of the metal in photocells, as a filter of X-rays, and for electrical condensers.

The use of zirconium oxide in the porcelain industry, for enamels, for high dielectric insulators, as an addition to titanium oxide dielectrics, for crucibles, and in the glass industry is the subject of a large number of publications, which will not be taken up here in any detail. Youngman(218) gives general information along these lines. Due to its high melting point, 2,715° C., ZrO_2 is used in refractories. It has been proposed for crucibles

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

by Thomson(212) among others, but such crucibles generally break upon heating, probably due to an allotropic modification; the addition of MgO is said to help avoid this disadvantage. ZrO_2 is used as a flux in small quantities in the form of zircon ore, according to Kinzel(202), to liquify basic open-hearth furnace slags. The use in enamels(13), for high dielectric porcelain(217), and in super-dielectric rutile insulators is of considerable interest. The heat conductivity of zirconium oxide is said to be as low as that of quartz, and in addition the thermal expansion is very low(192). According to Cohn(194), zirconia can be fused to a transparent glass of slightly yellowish tinge; it has very great hardness and outstanding resistance to chemical agents, and resembles fused quartz.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

Digitized by Google

Original from
THE OHIO STATE UNIVERSITY

BIBLIOGRAPHY

General References

FRIEDHEIM, C. and PETERS, F. Gmelin-Kraut Handbuch der anorganischen Chemie. vol. 6, No. 1. Carl Winters, Heidelberg, 1928, pp. 1-67.

MARDEN, J. W., and RICH, M. N. Investigations of Zirconium, with Especial Reference to the Metal and Oxide. Bureau of Mines Bull. 186, 1921, 152 pp.

MELLOR, J. W. A comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. 7, Longmans, Green, & Co., London, 1927, pp. 98-173.

VAN ARKEL, A. E. Reine Metalle. J. Springer, Berlin, 1939, pp. 191-207.

ULLMANN, F. Enzyklopadie der technischen Chemie. Vol. 10, Urban-Schwarzenberg, Berlin, 1932, pp. 765-772.

VENABLE, F. P. Zirconium and Its Compounds. The Chemical Catalog Co., New York, 1922.

Extraction from Ore

1. AGRIONATI, I. M. (Zirconium Dioxide.): Russian Patent 52,593, 1938; Chem. Abs., vol. 34, 1940, 5604.

Dissolution of eudialite in SO_2 solution and subsequent hydrolysis.

2. ALEXANDROV. G. P. (Decomposition of Zircon by the Chlorination Method.) Ukrainian Chem. Jour., vol. 11, 1936, pp. 287-297.

Chlorination of zircon mixed with carbon.

3. BOZEL-MALETRA, Soc. ind. prod. chim. (Purification of Zirconia.) French Patent 714,285, 1931.

Ignite at 400° C., and extract the iron with hydrochloric acid.

4. CERAMIC INDUSTRY. Zirconium Compounds. Ceram. Ind., vol. 32, No. 1, February 1939, pp. 41-42.

Methods of refining zirconia, and its use in refractories, pottery, and glass.

5. DEUTSCHE GASGLUHLICHT AUER GESELLSCHAFT. (Breaking up Zircon Ore.) French Patent 698,193, 1931.

Decomposition of zirconate with acids.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

6. _____. Treatment of Ores. British Patent 291,004, 1928.

The recovery of SO_2 from roasting sulfates and its reuse with fresh ores.

7. FRANCO-BREZILIENNE, SOC. MINIÈRE. (Preparation of Zirconium Oxide.) French Patent 650,937, 1929.

Melt ore with CaO or gypsum, extract with hydrochloric acid leaving insoluble zirconate; extract this with sulfuric acid.

8. HIORTDAHL, T. De l'action du zircon sur les carbonates alcalins et sur les chlorures alcalins. Bull. soc. chim., vol. 5, 1866, pp. 213-214.

The use of $CaCl_2$ as a flux for zircon.

9. IMPERIAL CHEMICALS IND. Preparation of Iron-Free Zirconia. British Patent 401,756, 1933.

Extraction from zirconate with acids.

10. KARL, A. (Preparation of Zirconia.) French Patent 677,621, 1930.

Sinter ore with soda ash and extract with acids.

11. KINZIE, C. I., and HAKE, D. S. Zirconium Oxides and Methods for Making Same. U. S. Patent 2,072,889, 1937. Method of Making Zirconium Oxide. U. S. Patent 2,168,603, 1939.

Thermal dissociation of zircon and the making of carbonitrides.

12. KINZIE, C. I., HAKE, D. S., EASTON, R. P., and EFIMOFF, V. V. Preparation of Zirconium Oxide. U. S. Patent 2,270,527, 1942.

13. KREIDL, N. J. Zirconium Oxide and Thorium Oxide in Ceramics. Jour. Am. Ceram. Soc., vol. 25, 1942, pp. 129-141.

14. LORENZ, C. (Preparation of Pure Zirconia.) German Patent 536,549, 1931.

Ore heated to above 1000° C., quenched, and separated by sliming.

Generated on 2024-09-19 15:44 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

15. MATIGNON, C. Action des températures élevées sur quelques substances refractaires. Compt. rend., vol. 177, 1923, pp. 1290-1293.

Thermal dissociation of zircon in a carbon resistor furnace.

16. MOISSAN, H. Sur la volatilisation de la silice et de la zircone et sur la réduction de ces composés par le charbon. Compt. rend., vol. 116, 1893, pp. 1222-1224.

17. RHENANIA-KUHNHEIM Verein Chem. Fabriken. Treating Zircon Ores. British Patent 287,424, 1928, and 282,023, 1928.

Sinter with CaO at 1,200° C., dissolve in HCl, precipitate $ZrOCl_2.8\ H_2O$ from concentrated $CaCl_2$ solution.

18. SCHMID, P. "Über die Gewinnung von Zirkonoxyd und "über die Konstitution einiger Zirkonsalze. Ztschr. anorg. Chem., vol. 167, 1927, pp. 369-384.

Use of CaO as a flux, and the extraction with hydrochloric or sulfuric acid.

19. SIMONOVA, L. K., FLEISHER, N. A., and BULKINA, M. L. (Hydrolysis of Zirconium Chloride.): Jour. Appl. Chem. (U.S.S.R.), vol. 11, 1938, pp. 941-945; Chem. Abs. vol. 33, 1939, p. 1888.

The conditions of oxychloride formation and precipitation.

20. TEICHMANN, L. and MARTINI, H. Zirconium Ore Treatment. British Patent 520,740, 1940, U. S. Patent 2,204,454, 1940.

Chlorination of ore, hydrolysis of the chlorides, and the use of acid for residue extraction.

21. THOMSON, J. G. A Preliminary Study of Zircite Ore. Jour. Phy. Chem., vol. 26, 1922, pp. 812-832.

Zircon plus carbon decomposed in an arc.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

Digitized by Google

Original from THE OHIO STATE UNIVERSITY

22. TRAPP, E. (Zirconia, Its Preparation and Uses.) Metallboerse, vol. 21, 1931, pp. 1516-1517 and 1565.

The sulfate process; alkali fusion, and the use in enamels.

23. TROOST, L. Sur la preparation du zirconium et du thorium. Compt. rend., vol. 116, 1893, pp. 1227-1230. Sur l'extraction de la zircone et de la thorine : Compt. rend., vol. 116, 1893, pp. 1428-1429.

Volatilization of silica and production of carbide.

24. ULLMANN, F. (Encyclopaedia of Technical Chemistry.) Urban Schwarzenberg, Berlin, 1932, vol. 10, pp. 765-772.

25. YUZ'KO, S. (Zirconium Oxide.) Russian Patent 53,758, 1938; Chem Abs., vol. 34, 1940, p. 5604.

Eudialite dissolved in hydrochloric acid and precipitated with SO_2.

26. ZINTL, E. Siliciummonoxyd : Ztschr. anorg. Chem., vol. 245, 1940, pp. 1-7.

27. ZINTL, E., and GRUBE, H. Reduction of Inorganic Oxidic Compounds by Silicon Monoxide. U. S. Patent 2,286,663, 1942.

Reduction of the silica content of zircon from 22 percent silicon to less than 0.5 percent.

PRODUCTION OF ZIRCONIUM METAL

28. ALEXANDER, P. P. Method for Reduction of Refractory Metals. U. S. Patent 2,038,402, 1936.

Calcium hydride and zirconia treated in a vacuum.

29. BALKE, C. W. Pure Columbium. Am. Electrochem. Soc. Prepr. 85-3, 1944, 6 pp.

Reaction of columbium carbide and columbium oxide in a vacuum to produce the metal.

Generated on 2024-09-19 15:44 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

30. BERZELIUS, J., (Zirconium Obtained by the Reduction of Potassium-zirconium Fluoride. Pogg. Ann., vol. 4, 1825, pp. 121.

Reduction of 2 $KF \cdot ZrF_4$ with potassium.

31. BOZEL-MALETRA, Soc. Ind. Prod. Chim. Preparation du carbure de zirconium. French Patent 714,283, 1931.

ZrO_2 and carbon reduced in the arc.

32. BRADT, W. E., and LINFORD, H. B. The Electrolysis of Aqueous Solutions of Sodium and Zirconyl Sulfates. Trans. Am. Electrochem. Soc., vol. 70, 1936, pp. 431-439.

Electrolytic deposition of a small amount of metal from aqueous solutions.

33. BURGERS, W. G. See van Arkel, A. E., Reine Metalle. Julius Springer, Berlin, 1939, p. 192.

Deposition of zirconium on a zirconium wire.

34. COOPER, H. S. The Preparation of Fused Zirconium. Trans. Am. Electrochem. Soc., vol. 43, 1923, pp. 215-230.

Reduction of $ZrCl_4$ with sodium in a vacuum and fusion of the metal in a vacuum Arsem furnace.

35. DAWIHL, W. Studien im Gebiete hoher und höchste Temperaturen. Tonind. Ztschr., vol. 58, 1934, pp. 449-451, 463-465, 477-478, 485-487.

ZrO_2 and carbon reduced in the arc.

36. DE BOER, J. H., and FAST, J. D. (The Alpha-Beta Transition in Zirconium in the Presence of Hydrogen.) Rec. trav. chim. Pays-Bas, vol. 55, 1936, pp. 350-356.

Phase diagram Zr-H.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

37. _____ (Electrolysis of Solid Solutions of Oxygen in Metallic Zirconium. Rec. trav. chim. Pays-Bas, vol. 59, 1940, pp. 161-167.

Transference of oxygen to the anode.

38. _____ Hafnium. Ztschr. anorg. chem., vol. 187, 1930, pp. 193-208.

Dissociation methods of metal deposition.

39. _____ (The Influence of Oxygen and Nitrogen on the Alpha-Beta Transition of Zirconium.) Rec. trav. chim. Pays-Bas, vol. 55, 1936, pp. 459-467.

Raising of the transition point by oxygen and nitrogen and its resulting sluggishness.

40. _____ Näheres über Zirkonium. Ztschr. anorg. Chem., vol. 187, 1930, pp. 177-189; Darstellung von Zirkonium. German Patent 609,501, 1935.

Reduction of $ZrCl_4$ with sodium; reduction of ZrO_2 with calcium, with calcium plus sodium, and with magnesium; and reduction of 2 $KF \cdot ZrF_4$ with sodium.

41. _____ Über die Darstellung der reinen Metalle der Titan Gruppe durch thermische Zersetzung ihrer Iodide: Ztschr. anorg. Chem. vol 153, 1926, pp. 1-8.

Production of metals through dissociation of their iodides.

42. DRIGGS, E. H., and LILLIENDAHL, W. C. Method of Producing Rare Refractory Metals by Electrolysis. U. S. Patent 1 835 025, 1931.

Electrolysis of ZrO_2 in a fluoride bath.

43. FAST, J. D. Über die Herstellung der reinen Metalle der Titan Gruppe durch thermische Zersetzung ihrer Jodide. Ztschr. anorg. Chem., vol. 239, 1938, pp. 145-154.

Lower iodides in the dissociation process.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

44. FAST, J. D., and JACOBS, F. M. Ungewohnlich hohe Loslichkeit von Stickstoff und Sauerstoff in einigen Metallen untersucht an Zircon und Titan. Metallwirtschaft, vol. 17, 1938, pp. 641-664.

Action of oxygen on the transition point; 40 atomic percent of oxygen and 20 atomic percent of nitrogen soluble.

45. FISCHVOIGT, H., and KOREF, F. Experimente über das Anwachsen von Metall Kristallen von der Gas Phase. Ztschr. techn. Phys., vol. 6, 1925, pp. 296-298.

Zirconium deposited on tungsten.

46. FRIEDRICH, E., and SITTIG, L. Herstellung und Eigenschaften hochschmelzender niederer Oxyde: Ztschr. anorg. Chem., vol. 145, 1925, pp. 127-140; Herstellung und Eigenschaften von Nitriden. Ztschr. anorg. Chem. vol. 143, 1925, pp. 293-320.

ZrO produced from ZrO_2 and carbon.

47. HAGG, G. (X-ray Study of the Hydrides of Titanium, Zirconium, Vanadium, and Tantalum.) Ztschr. phy. Chem., Sec. B, vol. 11, 1931, pp. 433-454.

Five phases for zirconium; a solubility of 5 atomic percent in the alpha phase.

48. HUNTER, M. A., and JONES, A. The Reduction of Some Rare Metal Chlorides by Sodium. Trans. Am. Electrochem. Soc., vol. 43, 1923, pp. 215-230

Reduction of ZrCl with sodium in a bomb.

49. KIERNAN, W. P. Zirconium and Preparation Thereof. U. S. Patent 1 760 413. 1930.

Manufacture metal powder, degas in a vacuum, and sinter.

50. KROLL, W. J. Ductile Titanium.. Trans. Am. Electrochem. Soc., vol 78, 1940, pp. 35-47.

Titanium chloride reduced with magnesium.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

51. _____ Verformbare Titan Legierungen. Ztschr. Metallkunde, vol. 29, 1937, pp. 189-192.

Influence of impurities on the hot malleability of titanium.

52. _____ Verformbares Titan und Zirkon. Ztschr. anorg. Chem., vol. 234, 1937, pp. 42-50.

Reduction of ZrO_2 with a mixture of calcium plus calcium chloride under argon.

53. LELY, D., and HAMBURGER, L. Herstellung der Elemente, Thorium, Uran Zirkon und Titan. Ztschr. anorg. Chem., vol. 87, 1914, pp. 209-228.

Production of malleable zirconium by reduction with sodium in a bomb.

54. MARDEN, J. W. Reduction of Rare Metal Oxides. U. S. Patent 1,602,542, 1926.

Reduction of ZrO_2 with magnesium in a sealed vessel containing an inert atmosphere.

55. MARDEN, J. W., and RICH, M. N. Investigation of Zirconium with Especial Reference to the Metal and Oxide. Bureau of Mines Bull. 186, 1921, 152 pp.

Comprehensive survey of the methods of reduction in general.

56. NOWOTNY, H., WORMNES, E., and MORNHEIM, A. Unterschungen über die Systeme Al-Ca, Mg-Ca, und Mg-Zr. Ztschr. Metallkunde, vol. 32, 1940, pp. 39-42.

Magnesium-zirconium equilibrium diagram.

57. PHILIPS, N. V. Gloeilampenfabrieken, Precipitating Metals by Decomposition of a Gaseous Compound Thereof. British Patent 543 457, 1942.

58. PLOTNIKOV, V. A., and KIRICHENKO, E. I. (Electrolytic Deposition of Zirconium from Fused Salts.) Mem. Inst. Chem. Acad. Sci. Ukrain., U.S.S.R., vol. 6, No. 1, 1939, pp. 3-15.

Electrolysis of fused $AlCl_3$, KCl, NaF, and ZrO_2.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

59. PODSZUS, E. Reindarstellung sehr reaktionsfähiger Metalle und Metalloide. Ztschr. anorg. Chem., vol. 99, 1917, pp. 123-131.

Reduction of the double potassium fluoride with sodium to obtain 99.3 percent Zr.

60. ROHN, W. Darstellung der Metalle Si, Ti, Zr, Hf, Th, V, Cb, Cr, Mo. German Patent 600,369, 1933.

Reduction of the oxides by the carbides in a vacuum.

61. RUFF, O., and BRINTZINGER, H. Reduktion von Thor, Zirkon, und Titandioxyd. Zrschr. anorg. chem., vol. 129, 1923, pp. 267-275.

ZrO_2 reduced with sodium and with sodium plus calcium in a bomb.

62. SCHULZE, A. Umwandlungs Erscheinungen in sogenannten Halbleitern. Ztschr. Metallkunde, vol. 23, 1931, pp. 261-265.

Resistance measurement at the transformation point.

63. TROOST, L. Recherches sur le zirconium. Compt. rend., vol. 61, 1865, pp. 109-113.

Reduction of $ZrCl_4$ vapor with Al, Na, or Mg; reduction of the double fluoride with Al; reduction of the double chloride with Mg or Na: fusion electrolysis of the double fluoride and the double chloride.

64. VAN ARKEL, A. E. Darstellung von hochschmelzenden Metallen durch thermische Dissociation ihrer Verbindungen. Metallwirtschaft, vol. 13, 1934, pp. 405-408.

Dissociation method.

65. _____. Darstellung von reinem Titanium, Zirkonium, Hafnium, und Thoriummetall. Ztschr. anorg. Chem., vol. 148, 1925, pp. 345-350.

Dissociation of iodides; mixture of $ZrCl_4$, H_2, and CO used.

66. _____. Reine Metalle. Julius Springer, Berlin, 1939, p. 203.

Generated on 2024-09-19 15:42 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google

Digitized by Google

Original from THE OHIO STATE UNIVERSITY

67. VON ZEPPELIN, H. Process for Producing Zirconium Metal. U. S. Patent 2,214,211, 1940; Manufacture of Alloys. U. S. Patent 2,250,687, 1941; Darstellung von Zirkon. German Patent 704,933, 1939; Preparation du zirconium. French Patent 847,196, 1939; Darstellung von Zirkon durch Reduktion von $ZrCl_4$ mit Magnesium; Metall. Erz, vol. 40, 1943, pp. 252-254.

United States patents refer to the use of a definite ratio of alkali and chloride in the production of the metal, and the melting of the container in producing alloys. The foreign patents concern the use of a vacuum in the preparation of the metal.

68. WEDEKIND, E., and LEWIS, S. J. Studien über das Element Zirkon, I. Liebigs Ann., vol. 371, 1909, pp. 366-389; Studien über das Element Zirkon, II, Liebigs Ann., vol. 395, 1913, pp. 149-194.

Part I describes the reduction of 2 $KF \cdot ZrF_4$ with magnesium, and part II the reduction of ZrO_2 with calcium in an iron tube and the properties of the hyride and nitride.

69. WEINTRAUB, E. Preparation of Boron and Zirconium. British Patent 25 033, 1910.

Zirconium chloride and hydrogen introduced into an arc.

70. WEISS, L. „Verfahren zur Herstellung leicht ziehbarer Metall Niederschläge und zur Darstellung verformbahrer Drahte und Rohre. German Patent 314,791, 1919.

A hot wire method for the deposition of metals with or without the presence of a hydrogen atmosphere; the dissociation of tungsten chloride referred to especially, but all volatile compounds used in general.

71. WEISS, L., and NEUMANN, E. Darstellung und Untersuchung regulinischen Zirkoniums. Ztschr. anorg. Chem., vol. 65, 1910, pp. 248-278.

An aluminide made from aluminum and the double fluoride of zirconium treated in a vacuum arc.

72. ZWIKKER, C. Transformations of Zirconium and Titanium. Physica, vol. 6, 1926, pp. 361-366.

The action of oxygen on the transformation point.

Generated on 2024-09-19 15:42 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Zirconium Alloys

73. ALEXANDER, P. P. Zirconium Magnetic Alloy. U. S. Patent 2,184,769, 1939.

Fe-Ni-Co-Zr magnets heat-treated at 345°C.

74. ALLIAGES AUTOPROTÉGÉS. Aluminum-Magnesium Alloys. British Patent 503,953, 1939.

Corrosion-resistant alloys of magnesium, zirconium, and aluminum, with 0.05 to 3 percent zirconium and 10 to 96 percent magnesium.

75. ALLIBONE, T. E., and SYKES, C. The Alloys of Zirconium. Jour. Inst. Metals, London, vol. 39, 1928, pp. 173-189. Also, SYKES, C. The Alloys of Zirconium. Jour. Inst. Metals, London, vol. 41, 1929, pp. 179-190.

Alloys Ag-Zr, Al-Zr, Cu-Zr, Fe-Zr, Ni-Zr.

76. ANDRIEUX, J. L. Preparation de composés binaires par fusion ignée. Congr. Chim. Nancy, vol. 18, pt. I, 1938, pp. 124-127; Chem. Zentral. pt. II, 1939, p. 3023.

Fusion electrolysis of a mixture of silicate and ZrO_2.

77. BECK, A. Magnesium und seine Legierungen. J. Springer, Berlin, 1939.

Reference book on magnesium alloys.

78. BECKER, K. (The Physical Properties of High Melting Compounds.) Physikal. Ztschr., vol. 34, 1932, pp. 185-198.

Nature of zirconium carbide; its structure, density, hardness, etc.

79. BECKET, F. M. (Iron Alloy Constituted Essentially of Iron, Silicon, and Zirconium.): German Patent 400,199, 1924.

Zirconium-iron-silicon alloy.

80. BECKET, F. M. Process for Producing Zirconium Alloys. U. S. Patent 1,996,037, 1935. British Patent 427,076, 1935.

React ZrC with fresh ore rich in silica or with silicon.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

81. BELOZERSKII, N. A., AND OTHERS. (Alloying Columbium, Zirconium, etc., with Iron, Chromium, etc.) Russian Patent 54,976, 1939; Chem Abs. vol. 35, 1941, p. 2802.

Fusion electrolysis with metal cathode which dissolves through eutectic formation; a chloride-fluoride bath used.

82. BOEHLER, GEBR. (Steel for Objects with High Resistance Against Dynamic Stress.) Austrian Patent 154,648, 1938.

Carbon steels for shells and armor plates.

83. BOEKER, J. G. Hard Alloys. British Patent 499,763, 1939.

Carbides and nitrides with a binder.

84. BOSCH, R. (Electrode for Electric Discharge.) Swiss Patent 197,919, 1938.

Spark-plug metal with 0.01-0.2 percent Zr; 0.01-10 percent Mn, and the remainder Ni.

85. BOZEL-MALETRA, SOC. IND. PROD. CHIM. (Making Zirconium Alloys.) French Patent 818,473, 1937.

Calcium carbide added in making zirconium-silicon. Alloys made that are higher in zirconium than in silicon; iron-zirconium alloys also made.

86. BRAID, H. Dental Alloy. U. S. Patent 2,246,288, 1941.

Alloy of Cr-Mo-Co-W-Zr with 0.25 to 3 percent zirconium.

87. CAMAC, L. H. Alloy. U. S. Patents 2,228,513, 1942, 2,310,214, 1943.

Corrosion-resistant alloys: Mg-Al-Zr-Ti and Mg-Zr-Al.

88. COMSTOCK, G. F., and BANNON, R. E. Heat-Treated Copper Castings Alloyed with Zirconium and Beryllium. Metals and Alloys, vol. 8, 1937, pp. 106-109; French Patent 836,017, 1939.

Properties of copper-zirconium-beryllium alloys.

Generated on 2024-09-19 16:02 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

89. COOPER, H. S. Alloy. U. S. Patent 1,221,769, 1916; 1,277,046, 1918; 1,278,304, 1918; Canadian Patent 179,121, 1917.

Nickel-zirconium combinations with other metals as a cutting alloy.

90. DE BOER, J. H., and JONAS, G. B. Nickel-Alloy Electrode. Canadian Patent 405,674, 1942.

Alloy for electrodes in vacuum tubes containing 0.05 to 3 percent zirconium; the remainder nickel; gas-free and with a tensile strength of 24 kg. per sq.mm.

91. FINK, W. L., and WILLEY, L. A. Equilibrium Relations in Aluminum-Zirconium Alloys of High Purity. Trans. Am. Inst. Min. and Met. Eng., vol. 133, 1939, pp. 69-80.

Aluminum side of the aluminum-zirconium equilibrium diagram.

92. FRIEDRICH, E., and SITTIG, L. Herstellung und Eigenschaften von Carbiden. Ztschr. anorg. Chem., vol. 144, 1925, pp. 169-189.

Zirconium carbide made from ZrO_2 and carbon under hydrogen at 1,900° C.

93. GAUTHIER, G., (SOC. ALAIS FROGES ET CAMARGUE). Aliages du magnesium. French Patent 829,316, 1938; Beryllium-Containing Magnesium Alloys. U. S. Patent 2,224,151, 1940.

Grain-refining action of zirconium.

94. GEBHARDT, E. (The Systems Zinc-Titanium and Zinc-Zirconium.): Ztschr. Metallkunde, vol. 33, 1941, p.7.

Equilibrium diagram of zirconium-zinc.

95. GMELIN. Handbuch der anorganischen Chemie. 8th ed., Verlag Chemie, 1937, System 35, pp. 836-840.

Preparation, tensile strength, hardness, etc., of aluminum-zirconium alloys.

96. GOYLER, A. C. Alloy. U. S. Patent 2,213,207, 1940.

A centrifugal casting alloy of W-Mo-U-Cr-Zr, containing 0.25 to 7 percent Zr.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

97. HANSEN, M. Der Aufbau der Zweistofflegierungen. J. Springer, Berlin, 1936.

98. HARRINGTON, R. H. Double-Aged Copper-Base Alloys. U. S. Patent 2,275,188, 1942.

Double aging of alloys after cold work.

99. HARTMANN, M. L. Zirconium Carbide. U. S. Patent 1,576,275, 1926.

Zirconium carbide produced from zircon in an arc furnace under reducing conditions.

100. HENSEL, F. R. Contact. U. S. Patent 2,195,307, 1940.

Alloy mainly of silver with 0.1 to 13 percent zirconium for welding electrodes.

101. HENSEL, F. R. Welding Electrode. U. S. Patent 2,097,816, 1937.

Copper-zirconium alloy with 0.1 to 5 percent Zr; mechanical properties of the aged alloy given.

102. HENSEL, F. R., and LARSEN, E. J. Alloys. U. S. Patents 2,268,940, 1942; 2,161,468, 1939; 2,137,281, 1938. Copper-Base Alloy. British Patent 503,753, 1939.

Copper-zirconium-beryllium welding electrodes with lithium added and with iron group metals added.

103. HENSEL, F. R., LARSEN, E. J., and DOTY, A. S. Beneficial Effects of Zirconium in Cast Nickel-Silicon Bronzes. Trans. Am. Inst. Min. and Met. Eng., vol. 143, 1941, pp. 212-215.

Nickel castings degassed with zirconium.

104. HENSEL, F. R., LARSEN, E. J., and DOTY, A. S. Copper-Zirconium-Cadmium Bronze. Metals and Alloys, vol. 10, 1939, pp. 378-380.

Ternary copper-zirconium alloys; Cd-Li-Si-Mg.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

105. I. G. FARBEN A. G. Magnesium Alloys. British Patent 511,137, 1940; SOCETI. GÉNÉRALE DU MAGNESIUM. (Magnesium Alloys.) French Patent 845, 843, 1939.

Use of Pb, Ca, Zn, Cd, Ce, Ag, Tl, Th, Cu, and Bi and avoidance of Al, Si, Sn, Mn, Co, Ni, and Sb.

106. JELJUTIN, W., and GRIGORASCH, R. Gewinnung von Silicozirkon. Arb. Moskauer Stalin - Inst. Eisen, No. 12, 1939, pp. 59-79; Chem. Zentralb., vol. 110, pt. 2, 1939, p.4336.

Zirconium-silicon alloy made by reduction with carbon, aluminum, and carbon plus silicon; lime was added. 12.

107. KAMISHIMA, Y. Alloy Containing Zr and W for Principal Constituent: U. S. Patent 1,926,775, 1933; (Hard Metal Alloy Made by Fusion.) French Patent 721,267, 1932.

Zirconium-tungsten alloys with other metal additions.

108. KELLEY, M. Copper-Base Alloy. U. S. Patent 2,169,187, 1939.

Precipitation of hardened copper-zirconium-cobalt alloy for electrical purposes.

109. KOESTER, W., and MULFINGER, W. (The Systems of Cobalt with Boron, Arsenic, Zirconium, Columbium, and Tantalum.) Ztschr. Metallkunde, vol. 30, 1938, pp. 348-350.

Magnetic compound, Co_4Zr, found in the cobalt-zirconium system.

110. KROLL, W. Titanium Alloys. German Patent 718,822, 1942.

Ta-Zr alloy for light reflectors; also Ti, Mo, and W.

111. KRUPP, F. Permanent Magnet Alloys. British Patent 524,420, 1941.

Fe-Co-Ni-Zr magnet alloys with Al or Ti present.

112. LENTZ, D., and WOEKEL, E. (Solder for Parts of Vacuum Containers, Especially for Light Bulbs, Discharge Lamps, and Rectifiers.) German Patents 665,005 and 665,006, 1938.

Zirconium alloyed with iron or nickel for a welding metal; 16 percent zirconium.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

113. MAGNESIUM ELECTRON, Magnesium-Base Alloys. British Patent 533,264, 1941.

Use of molded pieces of $ZrCl_4$ with a density of 2 to 2.3.

114. McELROY, L. A. Cutting Tool. U. S. Patent 2,235,232, 1940.

Alloy of chromium, cobalt, and tungsten with 0.25 to 3 percent zirconium.

115. MEJERSSON, G. A. Carbide schwerschmelzbarer Metalle. Seltene Metalle (Russ.), vol. 4. No. 4, 1935, pp. 6-20; Chem. Zentral., I, 1936, 2520.

Properties of zirconium carbide.

116. MISCH, L. (Crystal Structure Examination of Some Beryllium Alloys.) Metallwirtschaft, vol. 15, 1936, pp. 163-166.

Structure of ZrB_2 as shown by X-rays.

117. MOISSAN, H., and LENGFELD, F. (A New Carbide of Zirconium.) Compt. rend., vol. 122, 1896, pp. 651-654.

Zirconium carbide made from zircon and carbon in an arc furnace.

118. MOTT, W. R. Volatilities of Refractory Material. Trans. Am. Electrochem. Soc., vol. 34, 1919, pp. 275-295.

Volatility of zirconium carbide.

119. NIPPES, E. F. Copper-Nickel-Zirconium Alloys. Metals and Alloys, vol. 13, 1941, pp. 294-300.

Copper, nickel, and zirconium alloys.

120. NOWOTNY, H., WORNES, E., and MORNHEIM, A. Untersuchungen der Systems, Al-Ca, Mg-Ca, and Mg-Zr. Ztschr. Metallkunde, vol. 32, 1940, pp. 39-42.

Magnesium-zirconium equilibrium diagram.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

121. OBINATA, I., and FAYASI, S. (Researches on the Complex Alloys of Magnesium Based on the Magnesium-Cadmium System.) Tetsu- to - Hagane, vol. 24, 1938, pp. 34-42; Chem. Abs., vol. 33, 1939, p.4943.

Corrosion resistance of cadmium-magnesium-zirconium and magnesium-zirconium alloys.

122. PHILIPS, N. V. Gloeilampenfabrieken. Copper Alloys. French Patent 836,017, 1939; Belgian Patent 427,304, 1938; British Patent 508,330, 1940; German Patent 691,138, 1940.

Copper-zirconium electrical conductors with 0.02 to 5 percent zirconium.

123. PHILIPS, N. V., Gloeilampenfabrieken. Resistance Wires. British Patent 330,280, 1930.

Alloy of 1.5 to 2 percent zirconium with aluminum to be used for cathodes vacuum tubes.

124. PILLING, N. B. and TALBOT, A. M. A. S. M. Symposium of Age Hardening. 1939, pp. 231-257.

Ni Zr age hardening.

125. POGODIN, S. A., AND OTHERS, (Constitution and Properties of Copper-Zirconium Alloys.) Compt. rend. acad. sci. U.S.S.R., vol. 27, 1940, pp. 670-672; Chem Abs. vol. 35, 1941, 1745.

Equilibrium diagram of copper-zirconium.

126. POGODIN, S. A., and SCHUMOVA, I. S. (Alloys of Copper with Zirconium.) Ann. secteur anal. phys.-chim., Inst. chim. gen. (U.S.S.R.), vol. 13, 1940, pp. 225-232; Chem. Abs., vol. 37, 1943, p.4350.

Equilibrium diagram of copper-zirconium.

127. PRESCOTT, C. H. Jr. The Equilibrium Between ZrO_2 and C and Their Reaction Products at Incandescent Temperatures. Jour. Am. Chem. Soc., vol. 48, 1926, pp. 2536-2550.

Dissociation pressure of ZrO_2-C established as 1 atmosphere at 1,930°K; crystal structure discussed.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

128. **RAFFLES**, F. (Permanent Magnet.) Belgian Patent 428 870, 1938.

Magnetic alloys; 10 percent Zr, 5 to 40 percent Ni, 5 to 20 percent Al.

129. RENAUX, L. Contribution a l'étude de la zircone. Diss. Univ. Paris-Vincennes (Pharmacy), 1910.

Calcium carbide as a reducing agent.

130. ROHN W. Valve Made of Co-Ni-Fe-Cr Alloy. U. S. Patent 2,246,078, 1941.

Co-Ni-Fe-Cr alloy plus Zr or Ti for exhaust valves in combustion engines.

131. RUTHARDT, K. (Platinum Alloys.): German Patent 670,897, 1939.

Platinum alloys with 0.05 to 5 percent zirconium that are corrosion resistant, stick well to porcelain, and can be used for electrical contacts.

132. SARBEY, M. D. Flashlamp. U. S. Patent 2,272,779, 1941.

Flashlamp alloy of aluminum, magnesium, and zirconium containing 0.5 to 15 percent zirconium.

133. SAUERWALD, F. Heat Treatment of Magnesium Alloys Containing Zirconium. U. S. Patent 2,212,130, 1940.

Heat treatment of a magnesium-zirconium alloy at 450° C.

134. SAUERWALD, F. Magnesium-Zirconium Alloys. U. S. Patent 2,286,311, 1942; Process for the Production of Zirconium-Magnesium Alloys. U. S. Patent 2,228,781, 1941.

Magnesium-zirconium alloys with 2.1 to 5 percent zirconium and a method of introducing zirconium powder into magnesium by stirring.

135. SCHAEFER, C., Tool Alloys: U. S. Patents 2,307,960, 1943, and 2,301,082, 1942.

Alloys of Fe-Cb-Ta-Zr and W-Ta-Cb-Ti-Zr with 10 to 40 percent zirconium used for cutting tools.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

136. SERI. SOCIETA ANON. PROC. PRIV. IND. ALLOYS. British Patent 517,083, 1940.

Alloys of copper, zirconium, and beryllium.

137. THUM, E. E. The Book of Stainless Steel. Am. Soc. Metals, 1935, pp. 261, 441.

Free-cutting sulfur steels and zirconium as a carbon neutralizer and an alloying element.

138. TROOST, L. Sur la préparation du zirconium et du thorium. Compt. rend., vol. 116, 1893, pp. 1227-1230.

Zirconium carbide made in the arc furnace from zircon plus carbon.

139. VAN ARKEL, A. E. Reine Metalle. J. Springer, Berlin, 1939.

140. VAN ARKEL, A. E., and DE BOER, J. H., Darstellung von reinem Titanium, Zirkonium, Hafnium, and Thoriummetall. Ztschr. amorg. Chem., vol. 148, 1925, pp. 345-350.

$ZrCl_4$ reacted with carbon and hydrogen.

141. VAN LIEMPT, J. A. (The Light of Combustion of Some Metals and Alloys.) Rec. trav. chim. Pays-Bas, vol. 58, 1939, pp. 423-431.

Flashlight powders of magnesium, aluminum, and zirconium.

142. VOGEL, R., and HARTUNG, A. (Ternary Diagram Fe-Zr-S.) Arch. Eisen., vol. 15, 1942, pp. 413-418.

Ternary diagram of Fe-Zr-S, showing the melting point of ZrS_2 as 1550°C.

143. VOGEL, R., and LOEHBERG, K. Das System Fe-Fe_3C-ZrC-Fe_3Zr_2. Arch. Eisen., vol. 7, 1934, pp. 473-478.

Ternary diagram, Fe-Zr-C.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

144. VOGEL, R., and TONN, W. Das Zustandsschaubild Eisen-Zirkon. Arch. Eisen., vol. 5, 1931-32, pp. 387-389.

Equilibrium diagram of iron-zirconium.

145. VOLKERT, G. Experimente über die Metallurgie der Zirkonium Legierungen. Metall. Erz, vol. 40, 1943, pp. 246-252.

Zirconium-silicon alloys produced by reduction with carbon; also with CaC_2.

146. VON ZEPPELIN, H. Manufacture of Alloys. U. S. Patent 2,235,508, 1941.

Zirconium dispersed in a flux.

147. ——— Manufacture of Alloys. U. S. Patent 2,250,687, 1941.

$ZrCl_4$ with magnesium in a copper container reacted in a salt bath.

148. WAINSTEIN, G. M. Versuch zur Gewinnung von Kohlenstoffhaltigem und kohlenstoff-freiem Ferrosilicozirkonium. Metallurg (Russ.), vol. 13, No. 9, 1938, pp. 17-23; Chem. Zentralb., vol. 110, pt. 1, 1939, p.1640.

Zirconium-silicon alloy produced by carbon and silicon reduction.

149. WALLBAUM, H. J. (The Systems of Iron-Group Metals with Titanium, Zirconium, Columbium, Tantalum.): Arch. Eisen., vol. 14, 1941, pp. 521-526.

Equilibrium diagram of iron-zirconium with manganese, cobalt, and nickel.

150. WARTENBURG, Von Hv., BROY, J., REINICKE, R. (The Reduction of Difficultly Reducible Metal Oxides with Hydrogen.) Ztschr. Elekrochem., vol. 29, 1923, pp. 214-217.

ZrO_2 reduced with hydrogen under pressure in presence of tungsten.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

151. WEDEKIND, E. (Zirconium Carbide from Natural Zirconium Oxide.) Chem. Ztg., vol. 31, 1907, pp. 654-655; über kolloides Zirkonsilizid. Ztschr. Chem. Ind. Koll., vol. 7, 1910, pp. 249-251.

Zirconium carbide made in the arc, and the combination of ZrO_2 and silicon to give ZrOSi.

152. ——— Zur Kenntnis der Darstellung von Zirkonerde. Ztschr. anorg. Chem., vol. 33, 1903, pp. 81-86.

ZrO_2 and carbon treated in the arc furnace.

153. WEISS, L. Untersuchungen über natürliches Zirkondioxyd. Ztschr. anorg. Chem., vol. 65, 1910, pp. 178-227.

Zirconium carbide produced from zircon.

154. WILKINS, R. A. and BUNN, E. S. Copper and Copper-Base Alloys. McGraw Hill Book Co., New York, 1943, pp. 291-293. DELMONTE, J. Beryllium and Its Alloys. Metals and Alloys, vol. 7, 1936, pp. 211-215.

Master alloys containing zirconium.

Zirconium Halides

155. ALEXANDROV, G. P. (Decomposition of Zircon by the Chlorination Method.) Ukrain. Chem. Jour. (U.S.S.R.), vol. 11, 1936, pp. 287-297.

Zircon and carbon mixture treated with chlorine gas.

156. BELOZERSKII, N. A., and FREIDLINA, B. A. (Electric Conductivity of Mixtures $ZrCl_4$ and NaCl and $CbCl_5$.) Jour. Appl. Chem. (U.S.S.R.) vol. 14, 1941, pp. 466-468.

157. BELOZERSKII, N. A., and KUCHEREMKO, O. A. (The Diagrams of State of the Systems $ZrCl_4$-NaCl and ZrO_2-$CaCl_2$.: Jour. Appl. Chem. (U.S.S.R.), vol. 13, 1940, pp. 1552-1555.

Compounds formed with 4NaCl and with 1 NaCl; no solution of ZrO_2 in $CaCl_2$.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

158. BURGESS, L. Separation of Aluminum, Beryllium, and Zirconium from their Ores. Trans. Am. Electrochem. Soc., vol. 47, 1925, pp. 317-325.

Carbides made in an arc furnace and treated with HCl.

159. DE BOER, J. H. Zirconium. Ind. Eng. Chem., vol. 19, 1927, pp. 1256-1259.

Extraction from the ore; purification; properties of the metal; the iodide process; double chlorides with phosphorus.

160. DE BOER, J. H., and FAST, J. D., Näheres über Zirkonium. Ztschr. anorg. Chem., vol. 187, 1930, pp. 179-184.

Chlorination of ZrO_2 with CCl_4.

161. FAST, J. D. Das auftreten niedrigerer Zirkonjodide bei der Herstellung. Ztschr. anorg. Chem., vol. 239, 1938, pp. 145-154.

Formation of lower iodides of zirconium.

162. FISCHER, W., GEWEHR, R., and WINGCHEN. W. Über eine neue Anordnung zur Dampfdruckmessung und über die Schmelzpunkte and Sättigungsdrucke von Skandium, Thorium, und Hafniumhalogeniden. Ztschr. anorg. Chem., vol. 242, 1939, pp. 161-187.

Action of $ZrCl_4$ on quartz.

163. FRIEND, J. A. N., COLLEY, A. T. W., and HAYES, A. T. W. The Vapor Density of $ZrCl_4$ (Zirconium Tetrachloride). Jour. Chem. Soc. London, 1930, pp. 494-497.

Investigation shows that dissociation starts at 500° C.

164. MOISSAN, H., and LENGFELD, F. Sur un nouveau carbure de zirconium. Compt. rend., vol. 122, 1896, pp. 651-654.

Chlorination of zirconium carbide.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

165. PHILIPS, N. V., GLOEILAMPENFABRIEKEN. Preparing Carbides with High Melting Points. British Patent 397,372, 1933, and French Patent 749,349, 1933.

Dissociation of $ZrCl_4$ on a hot carbon filament.

166. PICON, M. Propriétés chimiques des sulfures de zirconium. Compt. rend., vol. 197, 1933, pp. 151-153.

Chlorination of the sulfide with HCl and with chlorine.

167. RAHLFS, O., and FISCHER, W., Dampfdrucke und Dampfdichten von Beryllium und Zirkonium Halogeniden. Ztschr. anorg. Chem., vol. 211, 1933, pp. 349-367.

Vapor pressure, subliming, and melting points of $ZrCl_4$, $ZrBr_4$, and ZrI_4.

168. RUFF, O. and WALLSTEIN, R. Die Reduktion des Zirkontetrachlorids. Ztschr. anorg. Chem., vol. 128, 1923, pp. 96-116.

$ZrCl_4$ reduced to $ZrCl_3$ with aluminum.

169. _____, (Purification of Zirconium Ores or Zirconium Products.) German Patent 371,604, 1923.

Reactions of $ZrCl_4$ with aluminum and other metals, also with oxides, $ZrCl_4$ passed over ore to eliminate iron and titanium.

170. SCHMID, P. Über die Gewinnung von Zirkonoxyd und über die Konsitution einiger Zirkonsalze. Ztschr. anorg. Chem., vol. 167, 1927, pp. 369-384.

Study of oxychlorides.

171. SIMONOVA, L. K., FLEISHER, N. A., and BULKINA, M. L. (Hydrolysis of Zirconium Chloride.) Jour. Appl. Chem. (U.S.S.R.), vol. 11, 1938, pp. 941-945.

Hydrolysis of $ZrCl_4$ and precipitation of oxychloride.

Generated on 2024-09-19 16:02 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

172. STAEHLER, A., and DENK, B. (Contribution to our Knowledge of Zirconium Halogenides): Ber. Deut. chem. Gesell, vol. 38, 1905, p. 2611.

Zirconium carbide treated with chlorine gas.

173. TROOST, L., and HAUTEFEUILLE, P. Sur quelques reactions des chlorures de bore et de silicium. Compt. rend., vol. 75, 1872. pp. 1819-1821.

Reaction of ZrO_2 and $SiCl_4$ gives $ZrCl_4$ and a silicate.

174. VAN ARKEL, A. E., and DE BOER, J. H. Darstellung von reinem Titan, Zirkonium, Hafnium, und Thoriummetall. Ztschr. anorg. Chem., vol. 148, 1925, pp. 345-350.

Reaction of CO and $ZrCl_4$ on a hot filament.

175. WEDEKIND, E. Zur Kenntnis der Darstellung von Zirkonerde. Ztschr. anorg. Chem., vol. 33, 1903, pp. 81-86.

Zirconium carbide treated with chlorine gas.

Other Zirconium Compounds

176. ALEXANDER, P. P. Method for Production of Alloys. U. S. Patent 2,163,224, 1939; The Hydride Process. Metals and Alloys, vol. 8, 1937, pp. 263-264.

Use of ZrH_2 to make alloys.

177. ALLOYS, LTD. (Toronto). (Making Alloys of Copper, Nickel, Silver with Titanium and the Like.) French Patent 835,468, 1938.

Use of copper, silver, and nickel with a hydride.

178. BECKER, K. (The Physical Properties of High-Melting Compounds.) Physikal. Ztschr., vol. 34, 1932, pp. 185-198.

Zirconium nitride discussed.

179. COMSTOCK, G. F. and EFIMOFF, V. V. Incorporating Nitrogen in Alloy Steels. U. S. Patent 2 098 567, 1937.

Nitriding steels with a cyanonitride.

Generated on 2024-09-19 15:45 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

180. FRIEDRICH, E., and SITTIG, L. Herstellung und Eigenschaften von Nitriden. Ztschr. anorg. Chem., vol. 143, 1925, pp. 293-320.

Zirconium nitride produced from ZrO_2, carbon, and nitrogen at 1300°C.

181. HAGG, G. (X-ray Study of the Hydrides of Titanium, Zirconium, Vanadium, and Tantalum.) Ztschr. physikal. Chem., Sec. B. vol. 11, 1931, pp. 433-454.

Five phases in the hydride system; five atomic percent hydrogen soluble in alpha zirconium.

182. PICON, M. Sur les sulfures de zirconium. Compt. rend., vol. 196, 1933, pp. 2003-2006.

Identification of ZrS_2, Zr_3S_5, and Zr_2S_3; ZrO_2 reacted with H_2S.

183. SIEVERTS, A. and GOTTA, A. Über die Eigenschaften einiger Metallwasserstoffe. Ztschr. anorg. Chem., vol. 187, 1930, pp. 155-164.

Equilibrium pressure of hydride as a function of temperature. Density of the hydride as a function of the hydrogen content; maximum hydrogen content; heat of formation.

184. SIEVERTS, A., and ROELL, E. Zirkonium, Thorium, and Wasserstoff. Ztschr. anorg. Chem., vol. 153, 1926, pp. 289-308.

185. STROTZER, E. R., BILTZ, W., and MEISEL, K. Zirkoniumphosphide. Ztschr. anorg. Chem., vol. 239, 1938, pp. 216-224.

ZrP_2, ZrP, and Zr_3P identified.

186. STROTZER, E. R., BILTZ, W., and MEISEL, K. Zirkoniumsulfide. Ztschr. anorg. Chem., vol. 242, 1939, pp. 249-271.

Trisulfide, disulfide, sesquisulfide, and 0.75 sulfide obtained.

187. VAN ARKEL, A. E. Reine Metalle. J. Springer, Berlin, 1939, p. 203.

Generated on 2024-09-19 15:46 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

Uses of Zirconium and Its Compounds

188. ALEXANDER, P. P. Packing of Powdered Metals. U. S. Patent 2,284,551, 1942.

Metals packed in noble gas.

189. ALLGEMEINE ELEKTRIZITÄTSGESELLSCHAFT. (Increase of Performance of Mercury Boilers.) German Patent 650,665, 1937.

Zirconium used in mercury boilers to improve wetting.

190. ALLOYS, LTD.(Toronto). (Alloys.) French Patent 835,469, 1938, and Belgian Patent 427,095, 1938.

Copper alloys sintered with zirconium hydride to produce a copper-zirconium alloy.

191. BALKE, C. W. Production of Refractory Metals and Alloys. U. S. Patent 2,107,279, 1938.

Hydrides sintered in vacuo to make metals.

192. CERAMIC INDUSTRY. Zirconium Compounds. Vol. 32, No. 1, February 1939, pp. 41-42.

Use of zirconium compounds in pottery, enamels, and glass.

193. CHAMBERS, G. H. Zirconium. Metals and Alloys, vol. 4, 1933, pp. 199-201.

Use of zirconium as a primer for ammunition, and composition of flashlight powders.

194. COHN, WILLI, M. The Crystal Modifications of a Clear Fused Zirconia Produced in the Sun Furnace. Trans. Am. Electrochem. Soc., vol. 68, 1935, pp. 65-71.

195. DE BOER, J. H. (Electric Discharge Tube.) German Patent 550,178, 1932.

Zirconium parts of tubes held at different temperatures, and zirconium as a getter heated when the tube is used.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

196. ESPE, W., and KNOLL, M. Werkstoffkunde der Hochvakuumtechnik. Springer, Berlin, 1936.

197. FAST, J. D. Zirconium as a Getter. Foote Prints, vol. 13, 1940, pp 22-30.

A discussion of the gas absorbtion of zirconium.

198. FORREST, W. Flashlight Powder. British Patent 390,352, 1933.

Zirconium hydride in flashlight powder with magnesium and nitrates.

199. GILLETT, H. W. Some Features of Ductile Zirconium and Titanium. Foote Prints, vol. 13, 1940, pp. 1-11.

Summary of certain physical properties of zirconium; comparisons with titanium and tantalum; and discussion of possible commercial uses.

200. HUKOGAWA, S., and NAMBO, J. (Absorption of Gases by Zirconium and Its Application to Vacuum Tubes.) Electrotech. Jour. (Japan), vol. 5, 1941, pp. 27-30.

The gettering power of zirconium.

201. JONES, W. D. Obtaining Coherent Masses from Powdered Metals. British Patent 503,874, 1939.

Copper alloys sintered with zirconium hydride.

202. KINZEL, A. B. Method of Making Steel Treating Slags. U. S. Patent 2,027,868, 1936.

Use of ZrO_2 in basic open-hearth slags to make them more fluid and less corrosive.

203. KOLLIGS, H. (High Ohmic Resistance Made of an Insulating Body Bearing Thin Resistance Layer.) German Patent 482,363, 1929.

Thin layers of zirconium for electric resistance.

Generated on 2024-09-19 15:44 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

204. LIGHT METALS. Getter Metals. London, January 1944, p. 34; February 1944, p. 77.

Discussion of zirconium getters.

205. PHILIPS, N. V. GLOEILAMPENFABRIEKEN. (Electric Discharge Tube.) German Patent 528,384, 1931.

206. PHILLIPS, N. V. GLOEILAMPENFABRIEKEN. Electrolytic Condenser. British Patent 309,574, 1929.

Zirconium electrolytic rectifier.

207. PHILIPS, N. V. GLOEILAMPENFABRIEKEN. (Flashbulb.) French Patent 780,657, 1935.

Use of zirconium in flashbulbs.

208. PHILIPS, N. V. GLOEILAMPENFABRIEKEN. Spinnerets for Making Artificial Silk. British Patent 361,842, 1931; French Patent 707,260, 1931.

Zirconium as a material for spinnerets.

209. SABINE, G. B. Reflecting Power of Evaporated Metal Films in the Near and Far Ultraviolet: Phys. Rev., vol. 50, No. 4, p. 396.

Reflecting power of zirconium.

210. SARBEY, M. D. Flashlamp. U. S. Patent 2,272,779, 1943.

Use of an Al-Mg-Zr alloy in flashlight bulbs.

211. TELEFUNKEN GESELLSCHAFT FÜR DRAHTLOSE TELEGRAPHIE. (Electronic Lamps.) French Patent 821,705. 1937.

Use of zirconium parts at a definite temperature against hydrogen.

212. THOMSON, J. G., and MALLET, M. W. Preparation of Crucibles from Special Refractories by Slip Working. Nat. Bureau of Standards Jour. Research, vol. 23, 1939. pp. 319-327.

Zirconia crucibles.

Generated on 2024-09-19 15:43 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY

213. VAN ARKEL, A. E. **Reine Metalle.** J. Springer, Berlin, 1939, p. 203.

Use of zirconium in photocells, for BaO reduction, and for X-ray filters.

214. VAN LIEMPT, J. A., The Light of Combustion of Some Metals and Alloys. Rec. trav. chim. Pays-Bas, vol. 58, 1939, pp. 423-431.

Light emission of aluminum-zirconium alloys.

215. VIERKOETTER, P. (Process for Producing and Maintaining a Vacuum in Discharge Tubes.) German Patent 540,617, 1931.

Gettering in vacuum tubes.

216. WEDEKIND, E., and KREBS, C. Preparation of Flashlight Powders. British Patent 352,118, 1931; (Process for making Smokeless and Smell-less Rapidly Burning Flashpowders Rich in Spectral Lines.) German Patents 293,998, 1916, and 336,004, 1921.

Zirconium powder and nitrates mixed and used for flashpowder.

217. WESTINGHOUSE ENGINEER. A New Superior High-Frequency Insulation; Vol. 5, 1945, pp. 30-31.

Zirconia used as an electrical insulator.

218. YOUNGMAN, E. P. Zirconium. Bureau of Mines Inf. Circs. 6455 and 6456, 1931, 30 and 63 pp.

General information and data on domestic and foreign deposits.

Generated on 2024-09-19 15:47 GMT / https://hdl.handle.net/2027/osu.32435030643878
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from THE OHIO STATE UNIVERSITY